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MAGNETISM

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MAGNETISM

BY

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OF EMMANUEL COLLEGE, CAMBRIDGE

WITH A GENERAL PREFACE BY

O. W. RICHARDSON, F.R.S.

YARROW RESEARCH PROFESSOR OF THE ROYAL SOCIETY
NOBEL LAUREATE IN PHYSICS, 1928

WITH 20 DIAGRAMS



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PREFACE

IN this book I have aimed at describing briefly the present outlook on certain aspects of magnetism, mainly those concerned with the magnetic properties of materials. The general idea underlying the choice of subject-matter and the treatment is indicated in the introduction. As the book is intended primarily for those to whom the subject is not new, I have dealt at greater length with the more recent developments.

Extensive references would have been out of place, but where work since 1925 is considered, I thought the usefulness of the book would be increased by footnote references, which may be regarded as supplementing those in *Magnetism and Atomic Structure*. References to the earlier papers will be found in the books and articles mentioned in the note at the end, so that there should be no difficulty in following up any particular topic in greater detail.

The book is written in the hope that it will be useful as a general survey, and as an introduction to those who wish to carry out research on the subject; and also that it may suggest new points of view to those whose main scientific interests lie in other directions.

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November, 1929

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MAGNETISM

INTRODUCTION

SCIENCE is largely concerned with the relation of detailed facts to general principles. Its progress is marked not only by the discovery of new facts but also by the discovery of relations between facts apparently unconnected. The different branches of physics, such as light, electricity, magnetism, grew from investigations of different particular phenomena, and they could at first be regarded as completely independent. Now, however, that independence is lost, and in dealing with a special branch of physics, it is perhaps desirable to begin by considering briefly its place in the wider scheme. Also, as only a few aspects of magnetism will be treated in this book, the limitations which have been imposed in the choice of subject-matter will be indicated.

Among the 'laws' of physics Eddington has distinguished three types, identical, statistical and transcendental, which together embrace the whole of physics. The 'identical' laws are those characteristic of field physics. The extension of the general theory of relativity is leading to a synthesis in which both gravitational and electromagnetic 'fields' appear as manifestations of the structure of the space time world. With the aspects of magnetism which fall in this scheme, this book will not be primarily concerned. The field theories, comprehensive though they are, give no indication of a necessary existence of that discreteness which is actually found. The existence of atoms, electrons and quanta must at present be regarded as fundamental; it is the 'transcendental' laws which are concerned with

their behaviour. The aspects of magnetism to be treated here are for the most part those whose interpretation must eventually be found mainly in terms of these transcendental laws, though statistical laws are also involved.

An account will be given of the magnetic properties of materials, and it will deal mainly with the effect of magnetic fields on the state of magnetization. Secondary effects of fields, such as those on light emission and transmission, will only be dealt with briefly, and in so far as they bear on the main subject. With these limitations, it seems possible to give in a short space an account not only of the general principles but also of some of the detailed facts. It will be shown that, largely as a result of the work of the last few years, an enormous number of facts can be correlated in terms of those general principles which are gradually being built up to describe the spectroscopic behaviour of atoms and their interaction. Attention will be directed to problems which await further experimental and theoretical investigation.

Methods of measurement and experimental details will not be described, as they may generally be readily found elsewhere, and unless the descriptions are fairly complete they are of little value. The aim will be to give a reasonably systematic account of the subject within the limits imposed, assuming as known those fundamental facts which are to be found in the usual text-books.

If a historical order of treatment were followed, ferromagnetism would be considered first. The earliest magnetic observations made were those on the attractive power of magnetite for iron. The magnetic properties of iron and the phenomena of terrestrial magnetism formed the main subject-matter of magnetism till the beginning of the nineteenth century. The relation between electricity and magnetism was then discovered, and the field aspects of magnetism came into prominence. With Faraday's discovery that all substances were magnetic, though very feebly, in general, compared with

iron, the investigation of dia- and paramagnetism began. It proceeded with increasing accuracy as improvements in technique were made. Theory advanced hand in hand with experiment. Conclusions as to the magnetic properties of atoms were drawn, suggested by the macroscopic magnetic observations, interpreted in the light of electron-atomic theory. The quantum interpretation of the effect of a magnetic field in modifying the radiation emitted by atoms has made these conclusions more precise. It is only in the last few years that attempts have been made to measure directly, by the magnetic deviation of atomic rays, the magnetic moments of individual atoms.

As often happens, the phenomena which are the easiest to observe are the most difficult to interpret. An iron magnet is much more complex than an atom, and it is in terms of the behaviour of atoms that that of magnets must be explained. In the sequence adopted in this book the main lines of the historical order will be reversed. The magnetic properties of atoms will first be considered (Chapter I), and then diamagnetism (Chapter II), this being a general property of all matter. Paramagnetism (Chapter III) is a more special property, and, in connection with it, it becomes necessary to consider the interaction between atoms. This interaction plays a still more important rôle in ferromagnetics (Chapter IV). The elements themselves, excluding the ferromagnetics, can be formally divided into paramagnetics and diamagnetics, but generally they behave unlike typical members of those classes, and are most conveniently discussed separately. The recent work on the effect of strong magnetic fields on the electrical conductivity of the elements will also be briefly described, as it is not only full of interest in itself, but also has an important bearing on a number of the problems discussed in the book (Chapter V).

In dealing with a subject like magnetism it is not necessary to consider the foundations of atomic theory. There are, of course, many aspects of magnetism, par-

ticularly on the technological side, which have an interest and importance quite independent of atomic theories, or indeed of any theories at all. In attempting to correlate a mass of magnetic facts, however, it is necessary to go deeper, but not so far as to involve the consideration of another range of physics altogether. The starting-point is a conception of the atom indicated by experimentally inspired theory; this conception being, so to speak, a symbolical summary which covers a large range of facts, especially spectroscopic. The question at issue is then whether this conception is adequate to account for magnetic phenomena. It will be seen that to a large extent it is. Magnetism, however, may also react on atomic theory, particularly in connection with interaction problems, and in this way specific magnetic investigations make their special contribution to the general outlook of physics.

CHAPTER 1

MAGNETIC PROPERTIES OF ATOMS

OLD AND NEW QUANTUM MECHANICS

IN the earlier quantum theory of atomic structure, the extra-nuclear electrons of an atom were regarded as concentrated charges moving in orbits about the nucleus as centre of force. If this conception is to be retained, the stability of atoms indicates that the electrons, though accelerated, cannot radiate energy continuously as the classical theory would predict. Non-radiating 'stationary' states must be possible, and Bohr extended the original quantum theory to the fixation of these stationary states. For periodic systems the fundamental postulate may be expressed by the equation

$$\int p dq = nh \quad . \quad . \quad . \quad . \quad (1)$$

The integral is taken over a complete period; p and q are conjugated momentum and position co-ordinates, n is an integer, and h is Planck's constant. (For an electron describing a circular orbit, this is equivalent to stating that the angular momentum must be an integral multiple of $h/2\pi$.) With this postulate, certain of the orbits classically possible could be selected as 'allowed', and the associated energies calculated. Emission of energy occurs as monochromatic radiation as a result of a transition between two stationary states, and the second fundamental postulate relates the frequency of the radiation with the energy change.

$$h\nu = E_1 - E_2 \quad . \quad . \quad . \quad . \quad (2)$$

On the basis of the two postulates the general char-

actor of atomic and also molecular spectra could be accounted for; and in those cases where the mathematical difficulties of a many-body problem were not too great, or could be evaded (as for spectra of H and He^+ , and X-ray spectra) the calculated frequencies of the lines were in remarkable agreement with experiment.

Although a number of special difficulties were encountered, the success of the theory for a time seemed to justify the general underlying conception of atomic structure, which was gradually rendered more precise. It was, however, realized that the scheme as a whole was not self-consistent. In brief, the atom was built up of classical electrons which behaved unclassically.

A fresh approach to the general quantum problem was necessary, and this was provided by Heisenberg and Schrödinger, though in quite different ways; the results, however, are equivalent, and both matrix and wave mechanics are to be regarded as special aspects of a new quantum mechanics. This not only gives the results of the older theory, where that was correct, and clears away many of the special difficulties, but it also forms a self-consistent scheme. In particular, the newer outlook gives a more self-consistent symbolical scheme for the atom, although the conception of the atom seems to lose much of its former vividness, as precise interpretations of the symbols can only be given when they correspond to essentially observable quantities. The orbital picture of the atom at once loses its definiteness, for if the electron is regarded as a point charge, it cannot be said to have simultaneously a precisely determinable position and velocity. According to the interpretation adopted—which matters little—the hydrogen atom is regarded as a nucleus (or centre of force) surrounded either by a distribution of space charge, or by a field of probability, the probability of the electronic charge being within a definite region. The characteristics of the probability fields or space charge distributions for atoms generally are defined by the quantum numbers, so there is a close similarity between much

of the formal treatment of the older and newer theories, although the interpretations are different. It is, therefore, frequently convenient to speak, for example, of the quantum number associated with the 'orbital' angular momentum, though the term orbital should not be understood too literally. Bearing this in mind, a formal description will be given of the quantum characteristics of the atom, with particular reference to the deduction from them of the observable magnetic properties.

ELECTRONIC AND ATOMIC QUANTUM NUMBERS *

Each electron in an atom may be characterized by a total quantum number n , and a subsidiary quantum number l . The total quantum number is integral, and can have values 1, 2, 3, . . . For a given n , l may have values 0, 1, . . . ($n - 1$); l is equal to $k - 1$ where k is the azimuthal quantum number of the older theory. The value $l = 0$ corresponds, on the space charge interpretation, to a static spherically symmetrical charge distribution, with no associated angular momentum; while the values $l = 1, 2, 3, \dots$ correspond to 'stationary' axially symmetrical 'streaming' distributions, with associated angular momenta $lh/2\pi$. Rather loosely, l may be regarded as giving the 'orbital' angular momentum in Bohr units. To each electron must also be assigned a spin quantum number s , where $s = \frac{1}{2}$. A consideration of the multiplet structure of spectral lines, and the upbuilding of atoms by addition of electrons, showed, before the advent of the new mechanics, that it was necessary to attribute to the electron some kind of 'duplexity'. The difficulties were largely met by the hypothesis of Goudsmit and Uhlenbeck that the electron had an intrinsic spin moment equal to $\frac{1}{2} \frac{h}{2\pi}$ ($\frac{1}{2}$ in Bohr units), and an associ-

* For further details, see A. Sommerfeld, *Three Lectures on Atomic Physics* (Melhuken, 1926); F. Hund, *Linienspektren und periodisches System* (Springer, Berlin, 1927).

ated magnetic moment of $\frac{e}{2mc} \frac{h}{2\pi}$ (1 in Bohr units).

Dirac * has shown that these characteristics follow as natural consequences from the appropriate relativistic generalization of the quantum mechanical equations for the electron.

In an atom the constituent electrons add together their effects, so that the state of an atom as a whole is to be regarded as a resultant. An important principle in connexion with an atom building, which may be noted here, is that of Pauli, which states that in an atom no two electrons may have an identical set of quantum numbers. In the non-degenerate case, where a definite axis is defined by an external field, the four independent quantum numbers may be taken as n , l , m_l , and m_s , where m_l and m_s are the resolved values of l and s along the axis.

In considering the atom as a whole, it is convenient to differentiate the quantum numbers of the individual electrons by a suffix i . The atom has a resultant 'orbital' moment l , and spin moment, s ; each of these being vector sums (Σ_i) of the orbital and spin moments of the individual electrons.

$$l = \Sigma_i l_i, \quad s = \Sigma_i s_i = \Sigma \pm \frac{1}{2} \quad . \quad . \quad . \quad (3)$$

l is essentially integral, and s integral or half-integral. (As an example, if there are two electrons with $l_i = 1$ and 2, l can assume the values 3, 2, 1, and s the values 1, 0.)

The total angular momentum of an atom, indicated by the quantum number j , is a resultant of the spin and orbital moments.

$$j = |l + s| \text{ vect.} \quad . \quad . \quad . \quad (4)$$

Thus for $l = 2$, $s = 1$, j can take the values 3, 2, 1. In general j takes values ranging from $l + s$ to $|l - s|$ at intervals of 1. The maximum number of j values

* P. A. M. Dirac, *Proc. Roy. Soc.*, 117, 610 (1928).

associated with one l value is thus equal to $(2s + 1)$, and this gives the multiplicity r of the l state

$$r = 2s + 1 \quad . \quad . \quad . \quad . \quad . \quad (5)$$

This scheme accounts for the various types of spectroscopic terms. Once it was realized that a great simplification was introduced by regarding the frequency of a line as proportional to the difference of two 'terms', a classification of terms could be made on the basis of the spectroscopic results independently of any theory. The theory outlined enables the classification to be made consistently, and gives it significance.

SPECTROSCOPIC STATES, AND MAGNETIC MOMENTS OF ATOMS

When the atomic line spectra are analysed in the light of Bohr's second postulate (the frequency condition), a system of energy levels for the atom can be deduced. Transitions do not occur between all the levels, and it is the limitation on the transition possibilities—summarized in selection rules, which now have a firm theoretical foundation—that enables the levels to be classified. In the simpler cases, where the spectroscopic properties are primarily due to a single series electron—as in hydrogen and the alkali metals—the term or level characteristics are to be interpreted as characteristics of the single electron. The terms are classified as S, P, D, F . . . terms, and taking these to correspond to $k = 1, 2, 3, 4 \dots$ or $l = 0, 1, 2, 3 \dots$ transitions occur only between terms for which k (or l) differs by 1. Except for the S level, each level is double (that is, there are two possible states for the atom differing slightly in energy), and the sub-levels are distinguished by a suffix giving the quantum number j . In transitions, j may change by 0 or 1. The term characteristics are completely accounted for by the scheme outlined above. Terms occur for which $l = 0, 1, 2, 3 \dots$ (S, P, D, F . . . terms), and for each of these, since $s = \frac{1}{2}$, there are (except when $l = 0$) two possible values for j , namely $l + \frac{1}{2}$ and $l - \frac{1}{2}$.

In general, the selection rules are somewhat more complicated. For atoms in which the states depend on a number of electrons, it is still most convenient to classify the terms primarily according to the resultant l for the whole atom; and the terms are called S, P, D . . . terms according as $l = 0, 1, 2, \dots$. Possible j values range from $l + s$ to $l - s$; the maximum term multiplicity being $2s + 1 (= r)$. The general term may therefore be written rL_j . To take a particular example, the symbol $^4D_{5/2}$ specifies for the atom in that state the 'orbital' moment ($l = 2$) the spin moment ($s = 3/2$, since $2s + 1 = 4$) and the total moment ($j = 5/2$) all expressed in Bohr units. A considerable amount of information is thus conveniently given by the spectroscopic symbol specifying the state of the atom, information which is of importance in connexion with the magnetic properties. It is for this reason that the rather formal, and to those unfamiliar with it, possibly forbidding subject of spectroscopic nomenclature is discussed here.

The Zeeman effect provides the link between spectroscopic and magnetic properties. As is well known, spectral lines in general separate into components when emission takes place in a magnetic field, the separation in the normal effect being proportional to the field strength. This separation can be traced back to a separation of the components of a single l_j level which in the absence of a field have the same energy. The different components of a j level may be specified by a magnetic quantum number m , which can take values $j, j - 1, j - 2, \dots, -j$; m may be regarded as the resolved value of j in the direction of the field. Classically, according to Larmor's theorem, the effect of a magnetic field on the motion of an electron is equivalent to a precession, the frequency change being

$$\Delta\nu = \frac{eH}{4\pi m_e c} \quad \dots \quad (6)$$

where e, m_e are the charge and mass of the electron.

On the orbital model theory it may readily be shown that the energy change is given by

$$\Delta E = m h \Delta \nu_n$$

where m is the magnetic quantum number, and $\Delta \nu_n$ the 'normal' Larmor frequency change. The ratio of the magnetic to the mechanical moment for the intrinsic spin, however, is double that for the orbital moment; when this is taken into account, and the calculation is made with the new mechanics, the result is

$$\Delta E = m g h \Delta \nu_n \quad . \quad . \quad . \quad . \quad . \quad (7)$$

or, for the frequency displacement of a term

$$\Delta \nu = m g \Delta \nu_n \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

Here g is the 'splitting factor' giving the ratio of the magnetic to the mechanical moment for the atom; the formula for g was first given by Landé, on semi-empirical grounds, and was later deduced theoretically.

$$g = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad . \quad (8)$$

With these formulæ, and the selection rule that m may change by 0 or 1, the observations on the normal Zeeman effect are completely covered.

If μ is the resolved moment of the atom, the expression for the energy change may be written

$$\Delta E = \mu H$$

Comparing this with (6) and (7)

$$\mu = m g \frac{e h}{4 \pi m_0 c} \quad . \quad . \quad . \quad . \quad . \quad (9)$$

The values of $m g$ thus give the possible resolved magnetic moments of the atom expressed in Bohr units, $\frac{e h}{4 \pi m_0 c}$ being the magnetic moment due to the motion of an electron in an orbit with angular momentum $h/2\pi$.

In connexion with the ordinary magnetic properties of materials, it is the characteristics of atoms in their normal, unexcited states which are of importance. The

normal state is that of lowest energy corresponding to the spectroscopic 'ground term'. The ordinary line absorption spectrum is due to transitions from the ground level, while the ionisation potential is equivalent to the difference between the energy of the atom in the ground state and the state in which an electron is just removed from the atom. The ground term may be deduced from an analysis of the spectra; and it is also possible to predict the ground term when the number and character of the electrons in the atom are known. Small letters are used to specify the orbital character of the electrons; *s*, *p*, *d*, *f* . . . electrons are electrons for which $l = 0, 1, 2, 3$. . . Pauli's exclusion principle limits the number of electrons in a group with the same total quantum number. The total possible number in a group with the same n and l is equal to $2(2l + 1)$, giving 2, 6, 10, 14 for groups of *s*, *p*, *d*, *f* electrons. (Thus for $l = 1$ there are six distinct combinations of the orbital and spin magnetic quantum numbers, $m_l = 1, 0, -1$ and $m_s = \frac{1}{2}, -\frac{1}{2}$). The periodic properties of atoms are to be traced back to the way in which the electrons are arranged in these quantum groups. For a completed or closed group the resultant mechanical and magnetic moment is zero. When an atom has a magnetic moment, the presence of an incomplete electron group is indicated.

THE MAGNETIC DEVIATION OF ATOMIC RAYS

A direct test of the spectroscopic conclusions as to the possible resolved magnetic moments of atoms may be made by experiments on the magnetic deviation of atomic rays. When such experiments were begun by Gerlach and Stern in 1921, the theory was not in such an advanced state. The conclusion to be drawn from the space-quantization theory of Sommerfeld and Debye, when expressed in the form that an atom with a magnetic moment could only orientate itself with its axis in certain definite directions with respect to a magnetic field, certainly appeared very surprising. The 'dis-

crete orientation', if it could be directly confirmed, would be one of the most striking manifestations of quantum discontinuity. The fact that the experimental results were in agreement with the predictions gave a further indication of the need for an outlook, such as that now embodied in the new quantum mechanics, in which there is a complete breaking away from crude bar-magnet conceptions of the atom.

The principle of the experiments is very simple.* The element under investigation is heated in an oven (see Fig. 1) and the issuing stream of atoms, delimited by slits, passes through a non-homogeneous magnetic field (obtained by wedge-slit pole pieces, shown in cross-section at E) and is received on a plate. The whole apparatus is in an enclosure in which a high vacuum can be maintained.

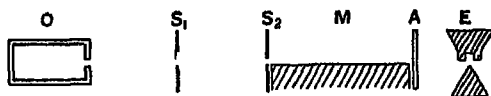


FIG. 1.—Diagram of Gerlach and Stern Apparatus

O, Oven. S_1 , S_2 , Slits. M, Magnet Pole Piece. A, Receiving Plate. E, Elevation of Magnet Pole Pieces.

In the absence of a field there is a single line trace. When a field is applied the atoms will be deflected, the deflection being proportional to the resolved magnetic moment in the field direction. From the trace obtained, the resolved magnetic moments of the atoms can be determined.

The essential parts of the apparatus are quite small. In some experiments, the magnet pole piece was about

* A general account of the method and of the results obtained up to 1926 is given in *Magnetism and Atomic Structure*, Chapter IX. For details, see W. Gerlach and O. Stern, *Ann. der Phys.*, 74, 673 (1924); 76, 163 (1925), and the later series of papers in the *Zeits. für Phys.* contributed from the Hamburg Institute for Physical Chemistry by O. Stern, F. Knauer, A. Leu, E. Wrede and J. B. Taylor.

5 cm. long, the receiving plate 3 mm. square, and the oven 2 cm. long. As the deflections obtained are small, the parts must be very accurately aligned. For good results, an elaborate technique is necessary in which a large number of details have to be considered.

In the early experiments with silver the atoms were received on glass plates; in some cases, the traces were invisible until the layer of atoms was thickened by 'developing' the plate in a hydroquinone silver nitrate solution. Receiving surfaces of various kinds were used for different atoms.

The velocity of the atoms depends on the oven temperature. For atoms in equilibrium

$$\frac{1}{2}mv^2 = \frac{3}{2}kT$$

Some previous experiments of Stern showed that the mean velocity of atoms issuing through slits was somewhat greater than this; and as a good approximation, the mean value of v was taken as

$$v = \sqrt{3 \cdot 5 kT/m} \quad . \quad . \quad . \quad (10)$$

Let μ be the resolved magnetic moment of the atom, l the length of the wedge pole piece, and s the deflection. (The plate is placed immediately behind the magnet pole piece.) Since the force on the atom is equal to $\mu \left(\frac{dH}{ds} \right)$

$$s = \frac{1}{2} \frac{\mu}{m} \left(\frac{dH}{ds} \right) \left(\frac{l}{v} \right)^2 \quad . \quad . \quad . \quad (11)$$

This gives, for the gram atomic moment $M \left(= \frac{R}{h} \mu \right)$, using (10),

$$M^{-1} = \frac{1}{2} \cdot \frac{1}{s} \cdot \left(\frac{dH}{ds} \right) \frac{l^2}{3 \cdot 5 RT} \quad . \quad . \quad . \quad (12)$$

(This expression has to be corrected for the variation of the inhomogeneity $\frac{dH}{ds}$ of the field along the path of

MAGNETIC PROPERTIES OF ATOMS 15

a deflected beam.) The inhomogeneity is found by measuring H (from the change in resistance of a bismuth wire) and $H \frac{dH}{ds}$ (from the force on a bismuth wire of known susceptibility); the values being found for various distances from the edge of the wedge. (Typical values were $H = 17,500$ gauss, $\frac{dH}{ds} = 236,000$ gauss cm^{-1} at $\cdot 15$ mm. from the wedge.) The oven temperature T was measured thermoelectrically or optically.

On the classical theory atoms of moment μ_0 would be expected to give a broadened trace—since μ_0 can have any direction relative to the field—extending from $+s_0$ to $-s_0$ obtained by putting $\mu = \mu_0$ in (11). Taking into account the Maxwellian distribution, the trace would be most dense in the centre. On the quantum theory, in the simplest case ($\mu = mg = \pm 1$), when the field is applied the trace would be expected to split up into two. This was exactly what was found for silver.

An absolute measurement was made of the resolved magnetic moment of the silver atom. The result for the gram atomic moment was $M = 5,690$. This differs by only 2 per cent.—well within the experimental error—from the theoretical value (5,593) for the Bohr unit magnetic moment per gram atom. For other elements the apparatus could then be 'calibrated' by making an experiment with silver.

The results for the different elements investigated will now be described, the μ values found being compared with the theoretical mg values.

In the first column of the periodic table the following elements have been investigated: H, Li, Na, K; Cu, Ag, Au. All gave double traces, the separations corresponding to resolved moments for the atoms of $\mu = +1, -1$ (in Bohr units). This agrees with the mg values for the $^2S_{1/2}$ ground terms.

Hydrogen was investigated independently by Phipps

and Taylor,* and by Wrede. Hydrogen atoms may be produced in a long discharge tube (a Wood tube) under appropriate conditions, or by dissociating the molecules by means of a hot filament. A stream containing a fairly high proportion of atomic hydrogen is passed through slits in glass, and received on a plate coated with molybdenum trioxide. The atoms reduce the oxide, and so produce a visible trace.

The atoms of the second column have two s electrons, which in the normal 1S_0 state, constitute a completed group. For Zn, Cd and Hg no deflected traces are found. In the fourth column elements, the two p electrons do not form a completed group, but the total moment vanishes in the normal 3P_0 state. This is confirmed by the results for Sn and Pb.

Thallium (atomic number 81), in the third column, is analogous to aluminium in having one p electron in addition to completed groups. This gives a $^2P_{1/2}$ ground term, the mg values (from 8) being $+\frac{1}{2}$, $-\frac{1}{2}$. The earlier experiments gave a small separation in qualitative agreement with this; later experiments, by Leu, have provided quantitative confirmation.

In the fifth column Sb and Bi have been investigated. With Sb only an undeflected trace was obtained, owing to the beam consisting almost entirely of molecules. With Bi it was at first thought there was some asymmetry in the repelled and attracted beams; in Leu's experiments, however, a symmetrical splitting was obtained. The spectrum has not yet been completely analysed. A $^4S_{3/2}$ ground term is probable, which would give mg values of $\pm\frac{1}{2}g$ and $\pm\frac{3}{2}g$. The coupling relations are complicated, and theoretically it is only possible to say that g should lie between 2 and $4/3$. Leu obtained only two resolved traces, but he shows that the distribution of density is consistent with the presence of atoms with resolved moments in the ratio of 1:3, whose traces merge into each other. The measurements then indicate a g value of about 1.45.

* E. Phipps and J. B. Taylor, *Phys. Rev.*, 29, 309 (1927).

Nickel gave three clearly defined maxima corresponding to $\mu = 0$ and $\pm \mu_1$, with μ_1 somewhat greater than 1, and indications of atoms of higher moment. This is consistent with the spectroscopic ground term for nickel, 3F_4 , for which $g = 5/4$, giving as the mg values $\pm 5/4$ (0, 1, 2, 3, 4):

With iron, only an undeflected trace was obtained. From the odd multiplicity of the iron spectrum, an undeflected trace would be expected, but other traces would be expected as well. A 5D_4 ground term gives $mg = \pm 3/2$ (0, 1, 2, 3, 4). Difficulties were encountered owing to the rapid oxidation of the traces, so that the experiments were inconclusive, and should not be taken as indicating a breakdown in the spectroscopic theory.

Excluding Bi, Ni and Fe, the magnetic deviation experiments, independently of and in agreement with spectroscopic theory, give the following values for the resolved magnetic moments of atoms in their normal state—

Cu, Ag, Au ; H, Li, Na, K	$\mu = \pm 1$
Zn, Cd, Hg ; Sn, Pb	$\mu = 0$
Tl	$\mu = \pm \frac{1}{2}$

There are a considerable number of interesting points relevant to these experiments which might be discussed, but it is only possible to mention one or two of them. The fact that hydrogen has a moment of one Bohr unit was accounted for in a most straightforward manner on the orbital theory by attributing this moment to the motion of the electron with angular momentum $h/2\pi$ in the innermost orbit (the Bohr 1,1 orbit). The effective collision area of such an atom at right angles to the direction in which a magnetic field could be applied would differ according as to whether the field was present or not ; for, when a field was applied, the orbit, instead of being orientated at random, would orientate itself at right angles to the field. This was tested by Fraser,* in a most ingenious experiment, in

* R. G. J. Fraser, *Proc. Roy. Soc.*, 114, 212 (1927).

which he determined whether there was a change in the relative numbers of neutral atoms and protons which passed through a 'resting' gas when a magnetic field was applied. To within 1 or 2 per cent. there was no change. This indicates that as far as the electric charge is concerned, the hydrogen atom is spherically symmetrical. This is in agreement with the quantum mechanical conception of the atom and the attribution of the magnetic moment, for normal hydrogen, to the intrinsic spin of the electron.

With the older outlook, the problem presenting itself as to the time required for orientation could receive no really satisfactory treatment; a new light is shed on it by Heisenberg's principle of indeterminateness.* The determination of a resolved magnetic moment is equivalent to a determination of energy (since $E = \mu H$). The accuracy with which this can be done in the magnetic deviation experiments depends on the widths of the traces; and these depend on the width of the slits and on the wave length associated with the atoms ($\lambda = h/mv$). There is thus a probable error in the energy determination. There is also a probable error, depending on the length of the magnetic field and the velocity of the atoms, in fixing the time t to which this determination applies. It may be shown that the product of the ranges of indeterminateness of E and t is of the order h . This experimental impossibility of assigning exact simultaneous values to E and t is analogous to the impossibility of assigning exact simultaneous values to p and q (momentum and position) for a quantum system. E and t are conjugated variables, like p and q , and the matrix formulation of the relation between such variables (Bohr's first postulate appears in the form $pq - qp = h/2\pi i$) may be regarded as the exact symbolical representation of essential experimental uncertainty. Although the principle of indeterminateness was not explicitly stated until the advent of the new quantum theory, it is, in itself, a direct conclusion

* W. Heisenberg, *Zetts. fur Phys.*, 43, 172 (1927).

from the experimental facts. In particular, it becomes as meaningless to speak of the energy of a system at an instant, as of a frequency at an instant. The resolved magnetic moment of an atom has a precise meaning only with reference to the conditions under which it is measured. It is not necessary to imagine that a sudden 'change of orientation' takes place as an atom enters a magnetic field; theory and experiment determine a probability distribution of the atoms among different energy states, which varies as the atoms pass through the field. In cases of most practical importance, however, the atoms may be regarded as having resolved magnetic moments with the definite values indicated by the spectroscopic theory and by the magnetic deviation experiments.

It should perhaps be mentioned here that there is now definite evidence that the atomic nucleus may have a spin moment associated with it. Back and Goudsmit* have investigated the hyperfine structure of the lines of Bi, and have shown that it can be interpreted as indicating that the nucleus has an angular momentum of $4\frac{1}{2}h/2\pi$. Further experiments will enable the magnetic moment to be estimated. The alternation of intensities in the lines of bands of the molecular hydrogen spectrum indicates that the hydrogen nucleus, the proton, has a spin moment $\frac{1}{2}h/2\pi$. Though the proton and electron have the same 'mechanical' moments, however, the magnetic moments are probably inversely proportional to their masses; so that no indication of the magnetic moment of the proton would be obtained in the deviation experiments. If the Li nucleus has a magnetic moment, Taylor's deviation results show that it cannot be as great as a third of a Bohr unit. The nuclear magnetic moment must in general be very small, and it seems fairly certain that it cannot, as has been suggested, play a primary rôle in determining the magnetic characteristics of materials.

* E. Back and S. Goudsmit, *Zets. fur Phys.*, 47, 174 (1928).

CHAPTER II

DIAMAGNETISM

THEORY

FERROMAGNETIC substances, typified by iron, are distinguished by the high value of the magnetization which they may acquire, and by other special characteristics which will be considered later. Other substances may be divided into dia- and para-magnetics. For these the magnetization is in general proportional to the field, being in the same direction for paramagnetics and in the opposite for diamagnetics. Let I be the intensity of magnetization acquired in a field H ; the volume susceptibility κ , and the mass susceptibility χ are defined by

$$\kappa = \frac{I}{H} \quad \chi = \frac{I}{\rho H} \quad . \quad . \quad . \quad . \quad (1)$$

where ρ is the density. The magnetic moment is thus equal to κH per unit volume, or χH per unit mass. The differences in behaviour of dia- and para-magnetics in magnetic fields may be formally accounted for by attributing a negative susceptibility to diamagnetics and a positive to paramagnetics.

Shortly after the discovery of the 'universality' of magnetism by Faraday, a 'molecular current' theory of dia- and para-magnetism was developed by Weber. Paramagnetism was attributed to intrinsic molecular currents which gave the molecule a 'permanent' magnetic moment, and diamagnetism to molecular currents induced by the field. The induction effect, giving rise to a magnetic moment in the opposite direction to the field, would occur whether the molecules had a per-

manent moment or not. Some fifty years later the electron theory, which now had a firm experimental basis, was applied by Langevin,* to dia- and paramagnetism in a classical paper on the subject (1905). An atom was regarded as containing electrons moving in orbits about a centre of force, these orbital electrons providing the molecular currents of Weber. As Langevin's treatment does not depend on very specific assumptions, his results may be readily modified in accordance with the later quantum theory of atomic structure.

The magnetic moment associated with an electron moving in an orbit with angular momentum p is $ep/2mc$. (This is equal to eS/cT where S is the area of the orbit, and T the periodic time, corresponding to iS for the magnetic moment associated with a current circuit.) If the orbits do not balance magnetically, the atom will have a resultant magnetic moment, and this will give rise to paramagnetism; if the resultant moment is zero, a purely diamagnetic effect will be produced. It is this case which will be first considered, though it must be remembered that there will be a diamagnetic effect whether the atom has a resultant moment or not; when the atom has a moment, however, it will be seen later that it is of such magnitude that the paramagnetic effect is usually much greater than the diamagnetic.

When a magnetic field is applied to a system consisting of electrons moving in equilibrium about a relatively massive positive centre of force (the nucleus), Larmor's theorem shows that the effect is the same as that of imposing a precession about the direction of the field of angular velocity ω , where

$$\omega = - \frac{eH}{2mc} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

(The equations of motion of the electrons in the precessing co-ordinate system without the magnetic field are the same, neglecting terms in H^2 , as in the resting co-ordinate system with the field; provided that the

* P. Langevin, *Ann. de Chim. et phys.* (8), 5, 70 (1905).

electric field of force is symmetrical with respect to the direction of the magnetic field.) Let μ_e be the magnetic moment of one orbital electron, r the radius of the orbit, ω the angular velocity, r_1 , ω_1 the radius and angular velocity of the 'resolved' orbit with plane at right angles to the direction of the field; except for a circular orbit, r and r_1 vary.

$$\mu_e = \frac{ep}{2mc} = \frac{e\omega r^2}{2c} \quad . \quad . \quad . \quad (3)$$

When the field is applied

$$\begin{aligned} \Delta\mu_e &= \frac{er_1^2}{2c} \{(\omega_1 + \omega) - \omega_1\} = \frac{e\omega}{2c} \overline{r_1^2} \\ &= -\frac{eH}{4mc^2} \overline{r_1^2} \quad . \quad . \quad . \quad (4) \end{aligned}$$

For an atom containing N electrons

$$\Delta\mu_A = -\frac{e^2 H}{4mc^2} \sum_N \overline{r_1^2} \quad . \quad . \quad (5)$$

If an atom has zero initial moment, the atomic susceptibility, χ_A , is given by

$$\chi_A = \Delta\mu_A/H = -\frac{e^2}{4mc^2} \sum_N \overline{r_1^2} \quad . \quad . \quad (6)$$

For atoms which are spherically symmetrical $\sum \overline{r_1^2} = \frac{2}{3} \sum \overline{r^2}$. It is usually convenient to deal with the gram atomic susceptibility, χ_A , the product of the mass susceptibility and the atomic weight. Let Z be the number of atoms per gram atom (Avogadro's number)

$$\chi_A = \chi \times A = \chi_A \times Z = -\frac{Ze^2}{6mc^2} \sum_N \overline{r^2} \quad . \quad (7)$$

Substituting numerical values

$$\chi_A = -2.85 \times 10^{10} \sum_N \overline{r^2} \quad . \quad . \quad (8)$$

The theory which has been outlined applies primarily to 'mono-nuclear' systems, that is to atoms, or to ions in solids or solutions, in so far as these can be

regarded as independent. For such systems, the diamagnetic susceptibility, depending only on the dimensions of the systems, and not on their interaction, should not vary with the temperature. Using the methods of wave mechanics, the electronic system may be treated as a continuous distribution of space charge, and the same general results will hold. For systems with more than one centre of force, molecules, r^2 loses its simple meaning. For atoms (8) gives χ in terms of the area of the electronic orbits (or of the area of the region in which the density of the space charge is appreciable); for molecules it gives only an upper limit, which will be approached more closely, the closer the approach to spherical symmetry.

In reviewing the experimental results on diamagnetic susceptibilities, they will be ordered according to the definiteness of the quasi-independent atomic and molecular systems constituting the substances examined; for it is to these systems that the theory directly applies. The results will then be considered in relation to the theories of atomic and molecular structure. The theory cannot be directly applied in a satisfactory manner to the solid elements, and the consideration of these is deferred to a later chapter.

EXPERIMENTAL RESULTS—SIMPLE IONS AND ATOMS

For a definite polar salt, such as NaCl, which exists both in solution and in the solid state in the form of ions, the susceptibility may be regarded as the sum of the susceptibilities of the separate ions. The susceptibility is often most conveniently found from measurements on solutions, by correcting for the susceptibility of water. Let χ , χ_i and χ_w be the susceptibilities of the solution, of the salt and of water ($\chi_w = -0.72 \times 10^{-6}$), and C , the concentration of the salt. Then, generally

$$\chi = C\chi_i + (1 - C)\chi_w \quad . \quad . \quad . \quad (9)$$

This relation does not invariably hold exactly, for the

state of the salt may vary with concentration, owing to interaction with the solvent. For the halides which have been examined, however, the relation holds over wide ranges of concentration. If an estimate can be made of the relative contributions of the anion and the cation to the susceptibility of one particular salt, a series of ionic susceptibilities may readily be found, by comparing different salts with the same anion or cation. A comprehensive investigation of the halides of the alkali and alkali earth metals has been made by Ikenmeyer,* from which values of ionic susceptibilities were deduced in this way. His results, as forming a series obtained under similar conditions, will be considered.

For the gram molecular susceptibility (χ_m) of CsI Ikenmeyer found the value -95×10^{-6} .

$$\text{CsI} \quad \chi_m = -95 \times 10^{-6}$$

Now Cs^+ and I^- both have 54 electrons, which have an inert gas-like configuration, that of Xenon. The ions differ in the nuclear charge, 55 for Cs^+ , and 53 for I^- . Now for electrons in similar quantum states, the orbital radii vary inversely as the effective nuclear charge. Following an approximation previously used by Joos, it was assumed that the mean square radii, and hence the ionic susceptibilities (using (8)) were inversely proportional to the nuclear charges. This leads to the following values for the gram ionic susceptibilities.

$$\begin{array}{ll} \text{Cs}^+ & \chi_A = -45.75 \times 10^{-6} \\ \text{I}^- & \chi_A = -49.25 \times 10^{-6} \end{array}$$

(The symbol χ_A will be used both for gram atomic and gram ionic susceptibility.)

With these values as standards, values for the other ions were then deduced from the directly determined susceptibilities of the salts in solution. These are given in the following table, in which N is the number of electrons in the ion, Z the nuclear charge.

* K. Ikenmeyer, *Ann. der Phys.*, 1, 169 (1929).

TABLE I.
Gram Ionic Susceptibilities. — $\chi_A \times 10^6$ (Ikenmeyer).

$\begin{array}{c} Z \\ \swarrow \\ N \end{array}$	$N - 1$	$N + 1$	$N + 2$
10	F ⁻ 13.9	Na ⁺ 10.4	Mg ⁺⁺ 4.5
18	Cl ⁻ 20.4	K ⁺ 16.9	Ca ⁺⁺ 11.0
36	Br ⁻ 34.8	Rb ⁺ 31.3	Sr ⁺⁺ 25.4
54	I ⁻ 49.3	Cs ⁺ 45.7	Ba ⁺⁺ 39.9

The values are plotted in Fig. 2.

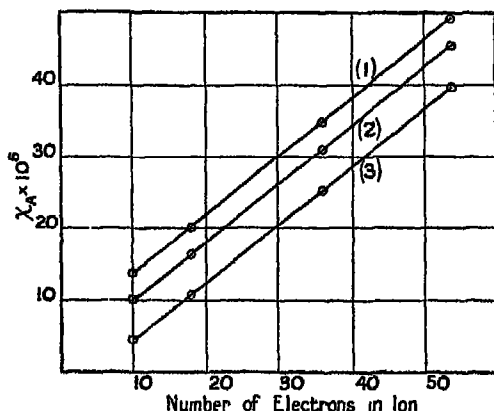


FIG. 2.—Gram Ionic Susceptibilities

— $\chi_A \times 10^6$ (Ikenmeyer)

(1) F⁻ — I⁻. (2) Na⁺ — Cs⁺. (3) Mg⁺⁺ — Ba⁺⁺

A critical discussion of experimental data would be out of place, but it should perhaps be noted that the ionic susceptibilities given by Ikenmeyer differ considerably in some cases from those given previously by Joos, but these had been deduced from much earlier measurements. Ikenmeyer's values are probably more

reliable, but the figures in Table I should not be considered as giving ionic constants with 'spectroscopic' accuracy. The results show, in the variation of susceptibility with electron number and ionic charge, that striking regularities appear when simple electronic systems are investigated. The values in Table I may be represented by the equation

$$-\chi_M \times 10^6 = c_1 N + c_2 \quad . \quad . \quad . \quad (10)$$

where c_1 (giving the slope of the curves in Fig. 2) is the same for the different series of ions, and c_2 varies.

$$c_1 = .80. \quad \text{Halogen ions } c_2 = 5.9.$$

$$\text{Alkali ions } c_2 = 2.4. \quad \text{Alkali earth ions } c_2 = -3.5.$$

(Extrapolation is not justifiable, as it would make the Be^{++} ion paramagnetic. For Li^{++} , Ikenmeyer gives $\chi_A = -4.0 \times 10^{-6}$, but this is very uncertain.) The equation shows that the mean square radius is approximately constant; neglecting the constants c_2 , the value obtained from (8) is

$$\overline{r^2} = \frac{.80 \times 10^{-6}}{2.85 \times 10^{10}} = (.53 \times 10^{-8})^2$$

This is of a reasonable order of magnitude, the radius of the innermost hydrogen orbit, on the Bohr theory, being $.532 \times 10^{-8}$ cm.

Until a few years ago there was great uncertainty as to the values of the ionic susceptibilities of the inert gases. For helium, $\chi_A = -46 \times 10^{-6}$ had been found, and for argon the value -246×10^{-6} had been deduced indirectly. It was pointed out by Joos (1923) that these values were completely incompatible with the general theory of atomic structure, and that the susceptibility of an inert gas atom should lie between that of the neighbouring positively and negatively charged ions with the same number of electrons. In the following table are given the data as to the ionic susceptibilities; the first number in each case being that given by Ikenmeyer, the second that deduced by Joos from measurements of Königsberger and others.

TABLE II.

Susceptibilities of Ions with the same number of Electrons as Inert Gas Atoms— $\chi_A \times 10^6$.

$\begin{array}{c} \text{Z} \\ \text{N} \end{array}$	$N + 1$	$N - 1$
He 2	Li 4.0 1.3	
Ne 10	Na 10.4 6.8	F 13.9 10.8
A 18	K 18.9 15.5	Cl 20.4 19.5

For the same electronic configuration, there should be a decrease in size, and hence in susceptibility, with increase in nuclear charge. Thus the susceptibility of A should be greater than that of K^+ and less than that of Cl^- . Though the variations in the experimental values for the ionic susceptibilities do not enable any exact estimates to be made for the inert gases, the order of magnitude to be expected is clear, and it differs widely from values which had previously been given.

A determination of the inert gas susceptibilities—an experiment involving skilled technique—was therefore carried out by Wills and Hector, using an ingenious manometric arrangement in which the gas could be balanced magnetically against a weakly diamagnetic solution. A gas pressure of several atmospheres could be used so that the volume susceptibility to be measured was increased. Special precautions were taken to ensure purity of the materials. The following results were obtained :

TABLE III.

Inert Gas Susceptibilities. — $\chi_A \times 10^6$ (Wills and Hector).

2 He	1.88
10 Ne	6.66
18 Ar	18.13

These values are in reasonable agreement with those to be expected from the ionic susceptibilities, and show that the inert gases do not behave anomalously; they suggest that Ikenmeyer's values for Li^+ and Na^+ are too high.

Discussion.—On the orbital theory, the mean value of r^2 for an n, k orbit about an effective nuclear charge Z is given by

$$\overline{r^2} = a_0^2 \frac{n^2}{Z^2} \left(\frac{5}{2} n^2 - \frac{3}{2} k^2 \right)$$

where $a_0 (= .532 \times 10^{-8})$ is the radius of the innermost (1, 1) orbit in hydrogen. This gives for the contribution of the orbit to the gram atomic diamagnetic susceptibility

$$\begin{aligned} \chi &= -2.85 \times 10^{10} \overline{r^2} \\ &= -.81 \times 10^{-6} \frac{n^2}{Z^2} \left(\frac{5}{2} n^2 - \frac{3}{2} k^2 \right) \quad . \quad (11) \end{aligned}$$

Atoms and ions will only be diamagnetic if the resultant spin and orbital momentum of the electrons is zero; or in general, if they are in a 1S_0 state, as are the ions and atoms for which results have been given above. If the effective nuclear charge is calculated from this expression for helium, with two electrons, from the observed susceptibility (-1.88×10^{-6}) it comes out as .93, which is, of course, much too small. Otherwise expressed, using a reasonable value for the effective nuclear charge, which may be estimated from the ionisation potential (about 1.7 for Z) the calculated susceptibility is much smaller than that observed. For more complicated atoms only very rough estimates of $\Sigma \overline{r^2}$ can be made from spectroscopic data; and all

that can be said is that there is agreement as to order of magnitude between the estimated and observed susceptibilities.

The expression corresponding to (11) with the new quantum mechanics has been calculated by Van Vleck * and Pauling,† with the result, for the gram atomic susceptibility

$$\chi_A = -81 \times 10^{-6} \sum \frac{n^2}{Z^2} \left\{ \frac{5}{2} n^2 - \frac{3l(l+1) - 1}{2} \right\} \quad (12)$$

In this expression l , the orbital quantum number, is equal to $k - 1$. The summation is taken over all the electrons in the atom, the appropriate effective Z being used for each. For the $(n1, 0)$ hydrogen orbit this gives a result three times as great as the old expression. The effective nuclear charge of Hc from the susceptibility comes out as 1.607, which is quite satisfactory.

Adopting the charge distribution conception of the atom, Pauling has evaluated the screening constant, and hence the effective nuclear charge, for the different groups of electrons in atoms, and using (12) has calculated the diamagnetic susceptibilities for inert gas like configurations. The calculated values agree fairly well with those observed, except for ions containing a large number of electrons for which the calculated values are much too large.

Pauling's calculations necessarily involve a number of rough approximations. For spherically symmetrical atoms Hartree ‡ has devised a 'self-consistent field' method with which the charge distribution satisfying the Schrödinger equation may be worked out much more precisely. For a number of ions and atoms he has given tables and curves showing the charge per unit radial distance (that is, in a spherical shell of unit thickness) as a function of the distance from the nucleus.

* J. H. Van Vleck, *Proc. Nat. Acad. Sci.*, 12, 662 (1926); *Phys. Rev.*, 31, 587 (1928).

† L. Pauling, *Proc. Roy. Soc.*, 114, 181 (1927).

‡ D. R. Hartree, *Proc. Camb. Phil. Soc.*, 24, 89 (1928).

It is possible to calculate the diamagnetic susceptibility corresponding to Hartree's charge distributions in a fairly simple manner.⁴ Let (dN/dr) be the charge, in electron units, per unit radial distance. The total charge, $\int_0^\infty (dN/dr)dr$, is then equal to the number of electrons in the ion. For the diamagnetic susceptibility

$$\chi_A = -2.85 \times 10^{10} \int_0^\infty r^2 \frac{dN}{dr} dr \quad . \quad (13)$$

This integral can most conveniently be evaluated graphically; from the $(r, dN/dr)$ curve, a curve giving $r^2 dN/dr$ against r is constructed; the area of this gives the required integral.

Curves for helium are shown in Fig. 3.

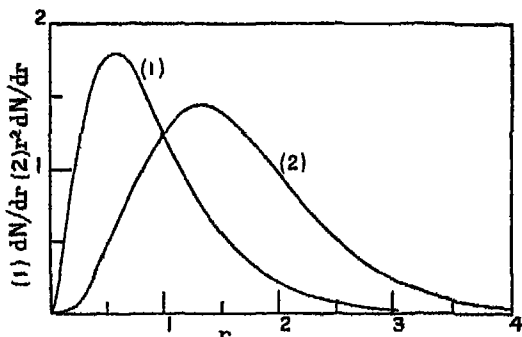


FIG. 3.—(1) Radial distribution of charge for He. dN/dr
(2) $r^2 dN/dr$
 r is measured in 'atomic units' ($\cdot 532 \times 10^{-8}$ cm.).

It is most convenient to express distances in atomic units ($\cdot 532 \times 10^{-8}$ cm.). Using this unit for r the susceptibility is given by

$$\chi_A = -2.85 \times 10^{10} \times (\cdot 532 \times 10^{-8})^2 \int_0^\infty r^2 \frac{dN}{dr} dr$$

* E. C. Stoner, *Proc. Leeds Phil. Soc.*, 1, 484 (1929).

$$-\chi_A \times 10^6 = .8066 \times \text{Area.} \quad . \quad . \quad . \quad (13a)$$

For helium this gives $\chi_A = -1.90 \times 10^{-6}$, a value which agrees remarkably closely with that observed. In the following table are given some further observed and calculated values.

TABLE IV.

Calculated and Observed Susceptibilities. $-\chi_A \times 10^6$.

	Calculated.		Observed.
	From Hartree Distribution.	Pauling.	
He	1.90	1.54	1.88
Na ⁺	5.47	4.2	10.4, 6.8 (Ne 6.7)
Rb ⁺	30.12	35	31.3
Cl ⁻	40.39	29	20.4, 19.5 (A 18.1)

For Na⁺ and Rb⁺, as well as for He, the values calculated from the Hartree charge distribution are in good agreement with those observed. (The susceptibility of Na⁺ should be slightly less than that of Ne, and the observed value for Ne is probably more accurate than those given for Na⁺.) For Cl⁻ however, the calculated value is much too large. This may be due to relatively small errors in the charge distribution for r large. Hartree states that the values are uncertain for $r > 532 \times 10^{-8}$ difficulties arising owing to the negative charge on the ion. Multiplication by r^2 , in calculating the susceptibility, greatly accentuates any errors in this region; the results indicate that the space charge is probably overestimated for r greater than about 1.5×10^{-8} cm.

Analysis of the X-ray scattering curves also shows that the distribution requires some modification. The calculation, however, is made for a free ion, and it may be that the different 'boundary conditions' for an ion in solution or in a crystal are sufficient to account for the modifications necessary.

Summarizing, it may be said that the observed values of ionic diamagnetic susceptibilities are in good general agreement with atomic theory. By the Hartree self-consistent field method, the approximate charge distributions in spherically symmetrical atoms and ions can be worked out, and from them theoretical values obtained for the susceptibilities. Accurate determinations of ionic susceptibilities will therefore provide an excellent test of the degree of accuracy of the calculated distributions, particularly for the outer parts of the ions, and so will supplement the X-ray scattering methods. Further work may be expected to yield much more precise information on the important question as to the difference in the charge distribution in free ions and those in crystals.

MOLECULES

The theory of diamagnetism which has been outlined applies strictly, as has been already stated, only to systems which are centro-symmetrical. For molecules whose resultant magnetic moment vanishes, however, equation (8) can still be used when the molecule approaches spherical symmetry, to give an upper limit for the susceptibility. In general the susceptibility of a molecule may be regarded as a sum of the contributions of the electronic systems associated with each nucleus, or as a sum of the atomic susceptibilities modified according to the way in which the atoms are joined together in the molecule. The susceptibility thus gives a rough indication of the 'size' of the molecule; that is, of the region through which the density of the space charge is appreciable.

To ensure that values characteristic of free molecules are obtained, it is necessary to make measurements on gases. The volume susceptibility of gases is proportional to the pressure, the molecular susceptibility being constant. Some experimental results, which were taken to indicate that at low pressures the volume susceptibility was three times as great as that deduced from a

linear relation, have now been shown to have been due to secondary experimental effects. It has been shown by Vaidyanathan * that generally, though not invariably, measurements of the susceptibility of a substance in the liquid and vapour state lead to approximately the same value for the molecular susceptibility.

In the following table are given the susceptibilities of a few of the simpler molecules, the measurements on liquids being due to Pascal, those on gases to Soné, Wills and Hector, and Vaidyanathan. The number of electrons in the molecule is also given.

TABLE V.
Gram Molecular Susceptibilities. $-\chi_M \times 10^6$.

N	From Gases.	N	From Liquids.
2	H ₂ 3.9	10	NH ₃ 19
14	N ₂ 7.4	26	C ₂ N ₂ 22.5
22	CO ₂ 18.7	26	CH ₂ Cl 33.5
42	C ₆ H ₆ 83	32	SO ₂ 19
		34	Cl ₂ 41.5
		42	C ₆ H ₆ 56

The values for benzene possibly provide an example of the wide difference which may be found with the liquid and the gas; but they have been obtained by different observers, and until more precise and extensive data are available, it would be premature to discuss the possible significance of such differences. In connexion with the more reliable values there are a number of points of interest.

In H₂ the spin moments of the two electrons neutralize each other. The diamagnetic susceptibility should be somewhat less than that of two H atoms—since the effective nuclear charge is greater. On the old quantum theory, for the H atom $-\chi_A \times 10^{-6}$ is equal to .81,

* V. I. Vaidyanathan, *Phys. Rev.*, 30, 512 (1927).

on the now to 2.43 (see Equations 11 and 12). The observed value for the molecule is thus incompatible with the old orbital model. In the space charge picture of the molecule, worked out by Heitler and London, the concentration of charge near the two nuclei falls off into an approximately ellipsoidal distribution about both. Treating the molecule as a pseudo-atom, the effective nuclear charge deduced from the susceptibility is 1.11, a reasonable value.

If Table V is compared with Table III (for the inert gases) it will be seen that the susceptibility of N_2 is only slightly greater than that of Ne, supporting the idea that the structure of N_2 corresponds to a single 'cube' or 'octet' of the Langmuir picture; or, that as far as the outer electrons (or outer parts of the electronic charge) are concerned, N_2 behaves as a pseudo-atom with a single centre of force. Cl_2 , on the other hand, has a susceptibility more than twice as great as A; the space charge distribution approximates to that which would be produced by joining together two argon like distributions. A consideration of these and other molecules shows that it is quite useless to look for simple general relations between susceptibilities and numbers of electrons and numbers of atoms in the molecules; but the diamagnetic susceptibility does assume significance when its indication of the molecular size is interpreted with reference to the chemical characteristics of the molecule. In some cases, of course, there are simple relations to be found; for molecules constituting electronic isomers, for example, Bhatnagar and others have shown that the diamagnetic susceptibilities are simply related to the effective radii of the molecules calculated from the radii of the atoms (from crystal structure data) assuming close packing; these relations, however, do not seem to have any deep significance.

The influence of chemical combination on magnetic properties has been studied by Pascal,* who made an

* P. Pascal, *Ann. de chim. et phys.*, 1908-13, and later paper in *Comptes Rendues*.

extensive series of measurements, particularly on organic liquids. He concluded that the molecular susceptibility χ_M could be expressed as a sum of the atomic susceptibilities χ_A with a correcting factor λ depending on the nature of the chemical linkages between the atoms.

$$\chi_M = \Sigma \chi_A + \lambda \quad . \quad . \quad . \quad (14)$$

Values were deduced for the susceptibility constants of atoms and groups, and for the correcting factors, which, substituted in (14), gave the observed molecular susceptibilities with an accuracy of 1 or 2 per cent. The following tables give examples of the values found.

TABLE VIa.

Susceptibility Constants. $-\chi_A \times 10^6$.

H	.	.	.	3.0	F	.	.	.	11.5
C	.	.	.	6.2	Cl	.	.	.	20
N	.	.	.	5.6	Br	.	.	.	31
O	.	.	.	4.6	SO ₂	.	.	.	37
Na	.	.	.	4	NO ₂	.	.	.	18
K	.	.	.	11	H ₂ O	.	.	.	13

TABLE VIb.

Constitutive Correcting Constants. $\lambda \times 10^6$.

Benzene	-	1.5
Ethylene	+	5.7
Diethylene	+	11.0
Acetylene	+	0.8

The correcting constant is sometimes positive. For ethylene this might be taken to indicate that the 'double bond' was paramagnetic, but its real significance becomes clear on considering a series of groups.

$$-\chi_M \times 10^6$$

$$\begin{aligned} -\text{CH}_2 - \text{CH}_2 &- (2 \times 6.2) + (4 \times 3.0) &= 24.4 \\ -\text{CH} = \text{CH} &- (2 \times 6.2) + (2 \times 3.0) - 5.7 &= 12.7 \\ -\text{C} \equiv \text{C} &- (2 \times 6.2) &- 0.8 = 11.6 \end{aligned}$$

On the views which have been outlined, the susceptibility gives an indication of the extent of the space charge distribution. The small susceptibility of the

ethylene as compared with the ethane group is therefore to be attributed to a concentration of the electronic charge and not to a paramagnetic effect of a double bond. In the ethane group each carbon atom may be regarded as forming the centre of an electronic distribution of the 'closed configuration' type, while in ethylene and acetylene the two carbon atoms approximate to a single centre for the outer part of the electronic charge. (In terms of the Langmuir model, ethane consists of two cubes, ethylene and acetylene of one.) Other apparent peculiarities can be explained in a similar way. In general, measurements of diamagnetic susceptibility show that in the maps of molecules provided by chemical formulae, double and multiple bonds represent regions in which two or more nuclei are drawn together, and where, in consequence, the electronic charge is more concentrated. (In terms of the orbital theory, the orbits of the electrons, in such regions, are reduced in area, and so contribute less to the susceptibility.) It would seem that diamagnetic susceptibility measurements might often throw a valuable sidelight on the structure of molecules and on the nature of chemical combination.

CHAPTER III

PARAMAGNETISM

THEORY

LANGEVIN'S Theory.—In a comprehensive investigation, Curie measured the susceptibilities of a large number of substances over a wide range of temperatures (1895). He found that, while the mass susceptibility of most diamagnetics varied little with temperature, that of paramagnetics decreased with increasing temperature. For oxygen the mass susceptibility was inversely proportional to the absolute temperature.

$$\chi = \frac{C}{T} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

This law of variation—Curie's law—was approximately obeyed by paramagnetic solutions. Langevin was the first to give a satisfactory theoretical interpretation of the main experimental results. His treatment of paramagnetism remains of fundamental importance, although it has to be modified in the light of later developments of atomic theory.

Langevin's theory applies essentially to a gas of which the molecules have a permanent moment due to circulating electrons. When a magnetic field is applied the molecules will tend to orientate themselves with their magnetic axes in the direction of the field. This tendency will be counteracted by the thermal motions, in particular the rotations, of the molecules, and there will be an equilibrium distribution of the axes with reference to the direction of the field—just as there is an equilibrium distribution of density for a column of

gas in a gravitational field. If the equilibrium distribution can be determined, an expression for the susceptibility may be deduced.

Let μ be the molecular magnetic moment (assumed to be the same for each molecule). Assuming equipartition of energy, the distribution of molecules among different states when equilibrium is attained may be calculated in the usual way; the number of molecules with axes making an angle θ with the field direction, per unit solid angle, will be proportional to $e^{\mu H \cos \theta / kT}$, the magnetic potential energy of the molecular magnet being $-\mu H \cos \theta$.

$$dn = Ce^{\mu H \cos \theta / kT} d\omega$$

The distribution of axes will be symmetrical about the field direction, and $d\omega$, the element of solid angle, may be taken as $2\pi \sin \theta d\theta$, this being the solid angle between two cones whose semi-vertical angles differ by $d\theta$.

$$dn = Ce^{a \cos \theta} \cdot 2\pi \sin \theta d\theta$$

$$\text{where } a = \mu H / kT$$

Let n be the total number of molecules, M the total magnetic moment, and $\bar{\mu}$ the mean resolved magnetic moment in the field direction.

$$\frac{\bar{\mu}}{\mu} = \frac{M}{n\mu} = \frac{\int_0^\pi Ce^{a \cos \theta} \cdot \mu \cos \theta \cdot 2\pi \sin \theta d\theta}{\mu \int_0^\pi Ce^{a \cos \theta} \cdot 2\pi \sin \theta d\theta}$$

The integrations may be carried out by putting $x = \cos \theta$, giving

$$\frac{\bar{\mu}}{\mu} = \frac{e^a + e^{-a}}{e^a - e^{-a}} - \frac{1}{a} \quad . \quad . \quad . \quad (2)$$

$$= \coth a - \frac{1}{a} \quad . \quad . \quad . \quad (2a)$$

When a is small (that is $\mu H \ll kT$), from the expansion of (2)

$$\frac{\bar{\mu}}{\mu} = \frac{a}{3} = \frac{\mu H}{3kT} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

The Langevin function is shown by the curve in Fig. 4.

It will be seen later that μH is generally much smaller than kT (except at very low temperatures), and the approximate expression (3)—represented by the tangent to the curve at the origin—may be used.

A magnetic field itself can only produce the precession effect discussed under diamagnetism. For paramag-

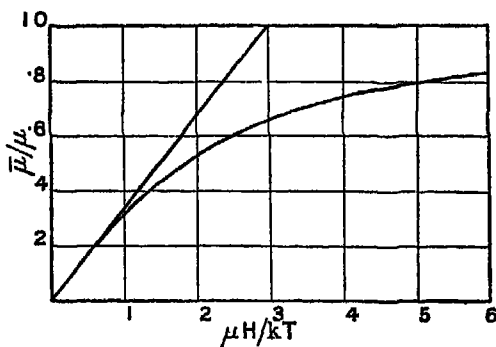


FIG. 4.— $\bar{\mu}/\mu$ as a Function of $\mu H/kT$

netism to occur, it is necessary, in order that the new equilibrium distribution may be set up when the field is applied, that there should be some 'mechanism' by which the appropriate changes in the energies and angular momenta of the molecules may be brought about. This mechanism might be provided by collisions, or by radiational processes.

From (3) an expression for the susceptibility may be derived. Let n_v , n_m and n_x be the number of molecules per unit volume, per unit mass and per gram molecule; n_x is Avogadro's number and is equal to mn_m where m is the molecular weight.

$$\left. \begin{aligned} \kappa &= \frac{n_1 \bar{\mu}}{H} = \frac{n_1 \mu^2}{3kT} \\ \chi &= \frac{n_m \mu^2}{3kT} \\ \chi_m &= \frac{n_m \mu^2}{3kT} = \frac{(n_m \mu)^2}{3(n_m k)T} = \frac{\sigma_0^2}{3RT} \end{aligned} \right\} \quad \dots (4)$$

The expression for χ_m is usually most convenient in discussing results, σ_0 being the gram molecular magnetic moment. The theoretical conclusion for a paramagnetic gas is thus completely in accordance with Curie's generalization (1), and the Curie constant assumes significance as being proportional to the square of the molecular magnetic moment. The Curie constant per gram molecule C_m is equal to mC where C is the constant per unit mass.

$$\begin{aligned} C_m &= mC = \sigma_0^2/3R \\ \sigma_0 &= \sqrt{3RC_m} \dots \dots \dots (5) \end{aligned}$$

According to Langevin's theory, the value of σ_0 which may be deduced from susceptibility measurements with ordinary fields is that corresponding to complete alignment of all the molecular magnets.

When α is small, $e^{\alpha \cos \theta}$ is approximately equal to $1 + \cos \theta$; the expression for $\bar{\mu}/\mu$ is then given by

$$\begin{aligned} \frac{\bar{\mu}}{\mu} &= \alpha \int_0^\pi \cos^2 \theta \sin \theta d\theta / \int_0^\pi \sin \theta d\theta \\ &= \alpha \overline{\cos^2 \theta} \dots \dots \dots (6) \end{aligned}$$

where the bar denotes a spatial mean value. When a 'continuous' distribution is possible, $\overline{\cos^2 \theta} = \frac{1}{3}$ —giving the expression (3). The quantum theory, however, necessitates a reconsideration of whether this continuous distribution can occur.

The Molecular Field.—The susceptibility of many solid paramagnetics does not vary with the temperature in the way indicated by Curie's law, but over consider-

able ranges of temperature, according to the relation

$$\chi = \frac{C}{T - \theta} \quad . \quad . \quad . \quad . \quad (7)$$

In Langevin's theory of a paramagnetic gas the molecules are supposed to exert no influence on each other depending on their orientation. Weiss extended the theory by supposing that the effective field H_e acting on a molecule was a resultant of the external field, H , and an internal field, H_i , proportional to the intensity of magnetization.

$$H_e = H + H_i = H + NI \quad . \quad . \quad . \quad (8)$$

If this internal field were of purely magnetic origin, N would be approximately equal to $4\pi/3$; but to account for observed susceptibilities, N must in some cases be thousands of times greater than this, and it is frequently negative. H_i , the 'molecular' field, must therefore be regarded as an interaction field whose origin remains to be explained, but which is equivalent in its effects to a magnetic field proportional to the intensity of magnetization. The consequences of the assumption may be worked out by substituting H_e for H in (3) for the case where $a(= \mu H_e/kT)$ is small.

$$\bar{\mu}/\mu = \mu H_e/3kT = \mu(H + NI)/3kT \quad . \quad (9)$$

For the gram molecular moment, since $I = \frac{\rho\sigma}{m}$ where m is the molecular weight, and ρ the density

$$\frac{\sigma}{\sigma_0} = \frac{\sigma_0}{3RT} \left(H + \frac{N\rho\sigma}{m} \right) \quad . \quad . \quad . \quad (9a)$$

$$\chi_m = \frac{\sigma}{H} = \frac{\sigma_0^2}{3R(T - \theta)} = \frac{C_m}{T - \theta} \quad . \quad (10)$$

$$\text{where } \theta = \frac{N\rho\sigma_0^2}{3Rm} = \frac{N\rho}{m} C_m$$

According to the Weiss equation (10), a paramagnetic substance in which there is a molecular field will have

a susceptibility varying inversely as the excess of the temperature above a certain critical temperature θ . This is known as the Curie temperature. For ferromagnetics the Curie temperature is positive (for iron about 1040° abs.), and above it ferromagnetism is replaced by paramagnetism. For most paramagnetics θ is small and may be positive or negative. The equation indicates that the inverse of the susceptibility varies linearly with the temperature

$$\frac{1}{\chi_M} = \frac{T}{C_M} - \frac{\theta}{C_M} \quad . \quad . \quad . \quad (11)$$

The slope of the $\frac{1}{\chi}$, T graph gives the Curie constant, which has the same significance as when $\theta = 0$; the intercept on the T axis gives θ from which the molecular field may be calculated. Although the value of θ obtained by extrapolation is frequently positive for paramagnetics, it cannot be concluded that the substance would become ferromagnetic at low enough temperatures, for there the linear relation between $1/\chi$ and T generally breaks down.

The Weiss Magnetron.—For paramagnetics which follow the Curie or Weiss law, the gram molecular magnetic moment may be calculated from the Curie constant, using (5). In 1911, from measurements then available, Weiss concluded that there was a fundamental unit of magnetic moment, the magneton, of which all atomic or molecular moments were multiples; the value of the Weiss unit moment per gram molecule (M_w) being 1123.5, corresponding to a value for the unit magnetic moment per molecule, the magneton, of 1.85×10^{-21} unit pole \times cm. Although later results have shown that the conclusions of Weiss cannot be maintained, the unit suggested is a convenient one. The magnetic moment as calculated from the Curie constant is usually expressed as p Weiss magnetons.

$$p = \frac{\sigma_0}{1123.5} = \frac{\sqrt{3RC_M}}{1123.5} \approx 14.07\sqrt{C_M} \quad . \quad (12)$$

The experimentally determined characteristics of a normal paramagnetic may thus be summarized by giving the values of p and l for the range of temperature over which it was investigated.

The Quantum Theory.—In the original form of Bohr's theory of atomic structure, the angular momentum p_ϕ was restricted to such values that

$$2\pi p_\phi = k\hbar \quad . \quad . \quad . \quad (13)$$

k being an integer. For the associated magnetic moment

$$\mu = \frac{e}{2mc} p_\phi = k \frac{e\hbar}{4\pi mc} \quad . \quad . \quad . \quad (14)$$

The quantity $e\hbar/4\pi mc$ is the natural quantum unit for magnetic moment. It is equal to 9.23×10^{-21} . This gives for the unit moment per gram atom

$$M_B = 5,593 \quad . \quad . \quad . \quad (15)$$

This is approximately five times as large as the Weiss unit

$$M_B/M_W = 4.967 \quad . \quad . \quad . \quad (16)$$

Since the Weiss unit was unsuccessful as a universal sub-multiple, a unit five times as large might seem somewhat unpromising. Consideration of the Zeeman effect showed, however, that some modification was necessary in the classical assumption that any orientation of the atomic magnetic axis with respect to the field was possible. That definite lines appeared in the Zeeman effect could, in fact, only be explained on a spatial quantization basis—by postulating that the resolved angular momentum in the field direction could only assume certain discrete values. The problem, however, was a complicated one, and it is only in the last few years that the facts have been co-ordinated by means of the relatively simple scheme outlined in Chapter I. A brief account will now be given of how a theoretical value for the atomic magnetic moment (the p value) may be obtained in terms of the quantum numbers defining the spectroscopic state.

Let j be the quantum number giving the angular moment of the atom as a whole, a resultant of l , the orbital, and s the spin moment. The resolved moment, m , in the direction of an applied field can have the values $j, j-1, j-2 \dots -j$, the corresponding magnetic moment, in Bohr units, being given by mg where g is the Landé splitting factor, a function of j, l and s (Chapter I, eq. 8). On the classical theory the resolved moment is equal to $\mu \cos \theta$ and can assume any value from $+\mu$ to $-\mu$; on the quantum theory possible resolved magnetic moments are confined to the mg values. Eq. (6) is therefore replaced by

$$\bar{\mu}/\mu = a(\overline{m/j})^2 \quad . \quad . \quad . \quad (17)$$

There are $2j+1$ values of m from $+j$ to $-j$.

$$\begin{aligned} \frac{\bar{\mu}}{\mu} &= a \frac{1}{2j+1} \frac{1}{j^2} [j^2 + (j-1)^2 + \dots + (-j)^2] \\ &= a(j+1)/3j \quad . \quad . \quad . \quad . \quad . \quad . \quad (18) \end{aligned}$$

Substituting $\mu H/kT$ for a , and g for μ , there results for $\bar{\mu}$, in terms of the Bohr unit μ_B

$$\bar{\mu} = \frac{g^2 j(j+1) \mu_B^2}{3kT}$$

Let M_B be the Bohr unit per gram molecule and n_M Avogadro's number

$$\chi_M = \frac{\bar{\mu} n_M}{H} = \frac{g^2 j(j+1) M_B^2}{3RT} \quad . \quad . \quad (19)$$

Now p , the Weiss magneton value, is calculated from the expression (cf. 12)

$$p = \sqrt{3RT\chi_M}/M_W$$

Substituting for χ_M

$$\begin{aligned} p &= (M_B/M_W) g \sqrt{j(j+1)} \\ &= 4.967g \sqrt{j(j+1)} \quad . \quad . \quad . \quad (20) \end{aligned}$$

In the simplest case, that of atoms in an S state, in

which the magnetic moment is entirely due to the electron spins, $g = 2$ and $j = s$. This gives

$$p = 4.967\sqrt{4s(s+1)} \quad . \quad . \quad (20a)$$

Possible values of s are $0, \frac{1}{2}, 1, 1\frac{1}{2} \dots$ corresponding to $0, 1, 2, 3 \dots$ 'unbalanced' electrons; the magnetic moment being $0, 1, 2, 3 \dots$ in Bohr units. From (20a), therefore, the p values corresponding to integral multiples of the Bohr unit may be calculated.

TABLE VII.
Magnetic Moments of Atoms in S States.

Spectroscopic State	$1S_0$	$2S_{1/2}$	$3S_1$	$4S_{3/2}$	$5S_2$	$6S_{5/2}$
Bohr Magnetons	0	1	2	3	4	5
p	0	8.6	14.1	19.3	24.4	29.4

These p values were first given by Sommerfeld, following on earlier work of Pauli, Epstein and Gerlach; they are in agreement as to order of magnitude with the experimental values for the ions of the first transition series, but since atoms and ions are not necessarily in S states, the more complete expression (20) has in general to be used. This expression was first given by Hund.*

In deriving (20) it has been assumed that all the atoms are in the same j state. This will not necessarily be true if the energy difference between different j states (corresponding to the same value of l and different values of s) is small compared with kT . This question has been discussed by Sommerfeld and Laporte,† and also by Van Vleck.‡ Let $\Delta\nu$ be the frequency difference

* F. Hund, *Zeits. für Phys.*, 33, 855 (1925).

† O. Laporte and A. Sommerfeld, *Zeits. für Phys.*, 30, 333 (1926).

‡ J. H. Van Vleck, *Phys. Rev.*, 31, 587 (1928).

between different j states. For $ch\Delta\nu \leq kT$, Van Vleck shows that l and s are not strongly 'coupled', but are quantized separately with respect to the field; (20) is then replaced by

$$p = 4.97\sqrt{4s(s+1) + l(l+1)} \quad . \quad . \quad (21)$$

This is a limiting expression for $\Delta\nu \rightarrow 0$ or $T \rightarrow \infty$, while (20) is the limiting expression for $\Delta\nu \rightarrow \infty$ or $T \rightarrow 0$.

Van Vleck's treatment of paramagnetism (and of diamagnetism) is on a rigorous quantum mechanical basis. A definite value can be assigned to the square of the magnetic moment. For the paramagnetic part, when the multiplet intervals are large, this is given by $\mu^2 = g^2 j(j+1) \mu_B^2$; the equations (19) and (20) are then derived directly by using the classical factor $1/3$ in the expression $\bar{\mu} = \frac{1}{3} \mu^2 H / kT$.

In the light of the general theory, which has been outlined, some of the experimental results will now be discussed, those for the simpler electronic systems being considered first.

SIMPLE IONS

As described in connexion with diamagnetism, ionic susceptibilities may be deduced from measurements on solid salts and solutions. It is found that paramagnetism makes its appearance as a characteristic property of ions which have an incomplete group of electrons, that is of ions of the various transition series of elements. In these, groups of electrons are incomplete for which $l = 2$ (d electrons—the complete group has 10) or, in the rare earths, $l = 3$ (f electrons—the complete group has 14). It is the ions of the first transition series, with from 19 to 27 electrons, which have been most completely investigated; data are also available for the rare earth ions.

Solutions.—The susceptibility of paramagnetic ions deduced from measurements on solutions (by correcting

for the diamagnetism of water, and of other ions present) generally follows the Curie law ($\chi = C/T$) closely over the necessarily restricted range which can be investigated; for concentrated solutions the Weiss law ($\chi = C/(T - \theta)$) must be used, though no simple generalizations have yet been found as to the way in which θ depends on the concentration or on the nature of other ions present. For not too concentrated solutions, the Curie law may be assumed to hold, and the ionic moment calculated on this assumption may be expressed as p Weiss magnetons (Equation 12). For a number of salts the 'apparent' p value varies very

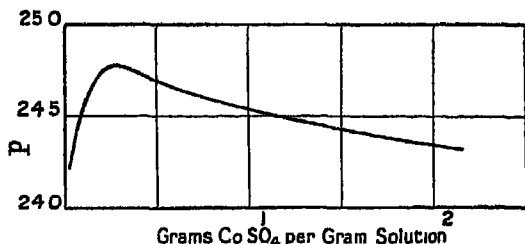


FIG. 5.—Variation of apparent Magnetic Moment of Co^{3+} with Concentration

little with concentration. For NiCl_2 , for example, the p value for the Ni^{++} ion is constant to within about .4 per cent. for concentrations ranging from .62 to 22.69 per cent., the value being 16.05–1.03. For cobalt salts, on the other hand, the p value for Co^{++} varies between about 24 and 25; the addition of acid may cause the apparent value to fall below 23. Some results for CoSO_4 are shown in Fig. 5.

Whether these variations indicate a change in the relative numbers of different magnetic 'carriers', or are due to the influence of the environment on the magnetic moment of ions of a single kind, will be discussed later. The important point which emerges from the measurements is that these variations are usually relatively

small, and that the p values deduced for a particular ion from measurements on solutions of different salts cluster closely round a fairly well defined value. Some results for the first transition series are shown in Table VIII (p. 49).

Solid Salts.—For the great majority of paramagnetic salts the Weiss law $\chi = C/(T - \theta)$ holds very closely over considerable ranges of temperature. The value of θ varies widely for different substances. Some examples of $1/\chi, T$ curves are shown in Fig. 6.

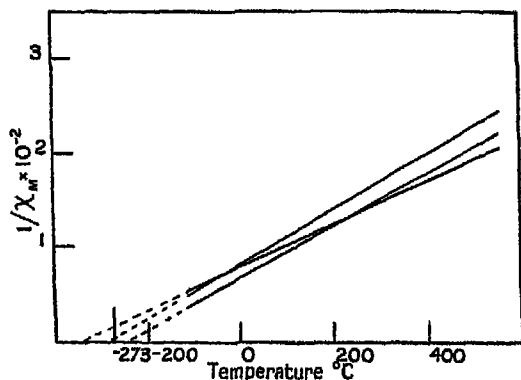


FIG. 6.—Variation of Susceptibility with Temperature

The graphs shown, from the highest to the lowest on the right, are those for

FeSO ₄	$p = 26, \theta = -16$
MnCl ₂	$p = 27, \theta = +21$
Fe ₂ (SO ₄) ₃	$p = 20, \theta = -73$

There are sometimes abrupt changes in the slope of the $1/\chi, T$ curves, attributable to changes in θ or C , possibly due in some cases to chemical changes. As for solutions, the p values deduced for the same ion in different salts generally agree fairly closely as to order of magnitude, though the variation may be considerable. Thus for the Co^{++} ion, Chantillon finds values ranging from 22 to 26.

TABLE VIII.
Calculated and Observed Magnetic Moments of Ions of the First Transition Series.

Number of Electrons	19	20	21	22	23	24	25	26	27
Ground Term . .	$^3D_{3/2}$	3F_3	$^4F_{9/2}$	5D_0	$^6S_{5/2}$	5D_4	$^4F_{9/2}$	3F_4	$^2D_{5/2}$
$4.97\sqrt{4s(s+1)}$. .	8.6	14.1	19.3	24.4	29.4	24.4	19.3	14.1	8.6
$4.97g\sqrt{j(j+1)}$. .	7.7	8.1	3.9	0	29.4	33.6	33.2	28.0	17.7
$4.97\sqrt{4s(s+1)+l(l+1)}$	14.9	22.2	25.8	27.2	29.4	27.2	25.8	22.2	14.9
Observed values of μ Solutions			Cr^3 18.2- 19.1	Cr^3 23.8	Fe^3 26-29.5 Mn^{2+} 29.4	Fe^3 26.5	Co^2 23-25	Ni^2 16.0	Cu^2 9-10
Solid Salts	V^4 8.9		Cr^3 18.9 Mn^{4+} 19.8		Fe^3 29 Mn^{2+} 27-30	Fe^2 25-27.5	Co^2 22-26	Ni^2 14.5-17	Cu^2 9-11

Collected Results.—The magnetic moments deduced from measurements on solutions and solid salts for the paramagnetic ions of the first transition series are shown in Table VIII. The positive charge of the ion is shown by the index. Ions with 18 electrons (K^1 , Ca^2) and with 28 (Cu^1 , Zn^2) are diamagnetic. A striking fact, first pointed out by Kossel, is that the p values for different ions with the same number of electrons (as Mn^{2+} and Fe^{3+}) are in close agreement. This is in accordance with the general theory, provided that the quantum state

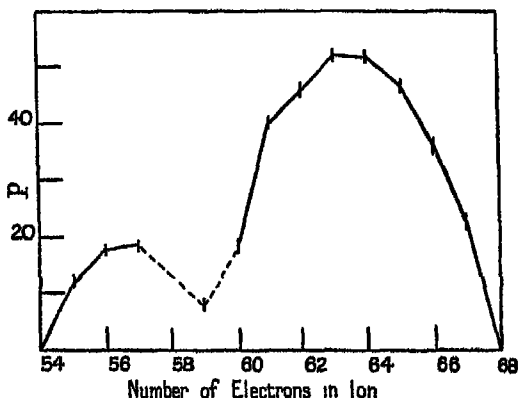


FIG. 7.—Rare Earth Ionic Moments

of the electrons in the ions is independent of the nuclear charge.

The susceptibilities of a number of rare earth sulphates and oxides have been measured by Cabrera and St. Meyer; and of aqueous solutions of various salts by Decker. The results for the ionic susceptibilities are in fair agreement. The p values for the ions (from La^3 54 to Lu^3 68) are plotted in Fig. 7.

For the ions of the remaining transition series only isolated data are at present available.

*Discussion.**—As outlined in Chapter 1, possible spectroscopic states for an ion may be determined when the number and quantum states of the electrons it contains are known. Of the possible states experiment and theory indicate that those with the highest resultant spin moment (s) will be deepest, and of those that with the highest resultant orbital moment (l). The j value corresponding to the deepest state (the ground state) is taken to be the lowest j in the first half of the group, and the highest in the second (corresponding to inverted multiplet intervals). Applying these considerations to the rare earth ions, which have varying numbers of f electrons ($l = 3$), Hund determined the ground states, and calculated the magnetic moments (using Eq. 20). The theoretical p values agree very closely with those found experimentally (Fig. 7) except in the case of Eu^{3+} for which the theory gives a zero moment. The expression used (20) is that corresponding to large multiplet intervals, which is appropriate for the rare earth ions.

In Table VIII are shown the spectroscopic ground terms for the ions of the first transition series. These have been deduced theoretically, but there is strong though indirect experimental evidence for them. The observed p values and those calculated from various theoretical expressions are shown in Fig. 8.

It will be seen at once that the observed values do not agree at all with those deduced using the expression which is satisfactory for the rare earths. (Curve 2. $p = 4.97g\sqrt{j(j+1)}$). It was suggested by Sommerfeld and Laporte that this might be due to the relative smallness of the multiplet intervals. For vanishingly small multiplet intervals the observed values should lie on curve 3 ($p = 4.97\sqrt{4s(s+1) + l(l+1)}$). Actually the observed values do not fall between the two 'limiting' curves. Bose† has developed the view that the

* For fuller discussion and references see E. C. Stoner, *Phil. Mag.*, 8, 250 (1929).

† D. M. Bose, *Zeits. für Phys.*, 43, 864 (1927).

paramagnetism of the ions is due entirely to the spin moment, the orbital moment playing no part. This leads to curve 1 ($\mu = 4.97\sqrt{4s(s+1)}$)—the same as that originally given by Sommerfeld as corresponding to whole number Bohr magnetons. Again the agreement is unsatisfactory, particularly for ions in the second half of the group; further, no reason is suggested

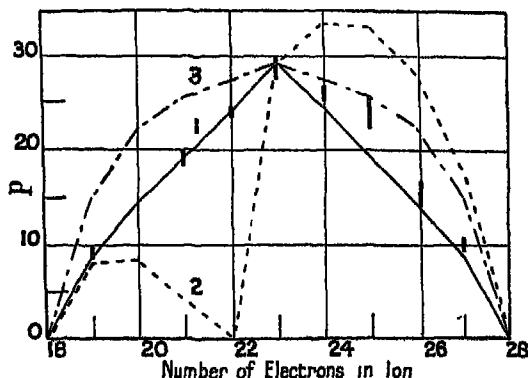


FIG. 8.—Calculated and Observed Magnetic Moments of Ions of First Transition Series

$$\text{Calculated} \begin{cases} 1. \text{ ————— } \mu = 4.97\sqrt{4s(s+1)} \\ 2. \text{ - - - - - } \mu = 4.97g\sqrt{j(j+1)} \\ 3. \text{ - . - . - } \mu = 4.97\sqrt{4s(s+1) + l(l+1)} \end{cases}$$

The thick vertical lines represent the range of observed values (see Table VIII).

as to why the orbital moment is inoperative in the first transition series, while it definitely plays a part in the rare earth ions.

In order to explain the facts it seems necessary to take into account the possibility of a definite interaction between the paramagnetic ion and surrounding ions and molecules. In the rare earth ions the effective electrons are not those of the group of highest quantum number.

Thus in Gd^{3+} 61 there is a closed group of eight electrons for which $n = 5$, while for the incomplete group of seven f electrons, $n = 4$. Interaction will presumably affect primarily the electrons in the group of highest total quantum number, and in the first transition series this includes the electrons responsible for the paramagnetism. Now Van Vleck's treatment shows that unless the spin and orbital moments are firmly coupled together (to give a resultant j) they should be considered separately. The symmetry of the electric charge distribution of an ion depends on the orbital moment l , and the definite way in which atoms and ions arrange themselves relatively to each other in a crystal suggests that there may be a strong ' l -interaction'. At the same time the s moment, depending on the intrinsic spins of the electrons may be relatively free. In the case of strong interaction, the s moment only may be affected by an applied magnetic field, the p value then being given by $p = 4.97\sqrt{4s(s+1)}$. When the interaction is weak, however, the l moment will also be affected. As will be seen from Fig. 8, the observed moments as a whole lie satisfactorily between the curves suggested as limits (curves 1 and 3) by these considerations; at the same time the difference in the behaviour of the rare earth ions is accounted for. While there are many details to be worked out it seems that the beginnings have been made in the explanation of a long-standing problem.

Low Temperature Investigations.—The magnetization of paramagnetics depends on H/T . With the magnetic fields attainable by the usual means, $\mu H/kT$ is small at ordinary temperatures; at sufficiently low temperatures, however, it may become large enough to enable the Langevin theory as to an approach to saturation to be directly tested. Octahydrated gadolinium sulphate, $Gd_2(SO_4)_3 \cdot 8H_2O$, with active ion Gd^{3+} 61, has been examined from this point of view by Onnes and his collaborators. Down to the lowest temperatures investigated (1.3° abs.) it follows Curie's law very closely, the susceptibility being given by

$$\chi = .0203/T$$

indicating a value for p of 39.2, corresponding to $\mu = 7.2 \times 10^{-20}$ (calculated classically). This gives

$$a = \frac{\mu H}{kT} = \frac{7.2 \times 10^{-20}}{1.37 \times 10^{-16}} \frac{H}{T} = 5.2 \times 10^{-4} \frac{H}{T}$$

With fields of 22,000 gauss at 1.3° values of a approaching 8 could be obtained. It was found that the magnetization was no longer proportional to the field, but that, within the limits of experimental error, the magnetization was related to the field in the way indicated by the Langevin curve (Fig. 4). The maximum intensity of magnetization obtained corresponded to 84 per cent. of the saturation intensity, calculated classically; or to about 95 per cent. of that calculated on the quantum theory for an ion with a moment of 7 Bohr magnetons. This provides an experimental proof that the saturation moment calculated from the susceptibility in small fields is at least approximately equal to the saturation moment which would be observed in very strong fields. It has seemed remarkable that solid gadolinium sulphate behaves in accordance with the theory for a paramagnetic gas—as though the gadolinium ions were free to rotate like gas molecules; it is, however, not necessary to suppose that a rigid ion rotates, but rather that the possible charge distributions associated with the ion in a field are such that the resolved magnetic moment can only have certain definite values.

The susceptibilities of a series of sulphates of iron, nickel and cobalt, both in powder form and as single crystals, have been measured by Jackson down to temperatures of 14° absolute. It was found that in general at low temperatures the $1/\chi$, T graphs were not linear, but showed curvatures of various types, indicative of 'cryomagnetic' anomalies. Foëx has given a qualitative explanation of these effects on a classical basis by assuming the existence of a potential energy depending on the orientation of the magnetic carrier with respect to the crystal lattice. The theory

may be brought into relation with the assumption of a quantum interaction field, but no quantitative treatment has yet been given. Further investigations, both experimental and theoretical, on paramagnetism at low temperatures will undoubtedly throw much light on many problems, particularly as to the interaction between an ion and its neighbours, which are at present very obscure.

The Weiss molecular field theory formally correlates many of the facts, but, as has already been pointed out, the field is not of magnetic origin. It arises in some way from the peculiarities in the quantum-mechanical interaction of electronic systems, and its discussion is best deferred until ferromagnetism is considered.

MOLECULES

The susceptibility of the paramagnetic gas oxygen has been measured over a wide range of temperatures by different observers, and it has been found to follow Curie's law very closely. The Curie constant, and hence the molecular moment, can therefore be deduced from measurements at a single temperature, of which the most accurate are probably those of Bauer and Piccard (1920), who also measured the susceptibility of nitric oxide. The results are shown in the following table:

TABLE IX.
Magnetic Constants of O_2 and NO.

	Mass susc. at 20° C. $\chi \times 10^6$	Vol. susc. 20° C. 760 mm. $\kappa \times 10^6$	χT	Gm. mol. Moment σ_0	Weiss Magnetons p
O_2	107.8	.1434	.0316	15,920	14.2
NO	48.7	.0807	.0143	10,330	8.2

The susceptibility of oxygen in the liquid and solid state has been determined by Perrier and Onnes. For the liquid mixed with feebly diamagnetic liquid nitrogen between 60° and 80° abs. the susceptibility is given by

$$\chi = \frac{.315}{T - \theta}.$$

The molecular field constant is negative

(indicating a negative molecular field) and varies with the concentration of the oxygen from -2.2° for 8.1 per cent. to -29.5° for 74.6 per cent. Solidification (at about 57° abs.) results in a sudden decrease in susceptibility, and a large increase in θ . At 33° a new allotropic modification is formed which has the anomalous characteristic that the susceptibility decreases with decreasing temperature down to 13° abs.

Nearly all gases are diamagnetic; this is due to the fact that most stable molecules contain an even number of electrons, which will usually give rise to diamagnetism. A solution of ClO_2 (33 electrons) in carbon tetrachloride is paramagnetic, the susceptibility corresponding to a magneton value of 8.7. NO_2 (23) is also paramagnetic, but the susceptibility has not been accurately determined. Ozone is diamagnetic.

The study of band spectra has shown that electronic levels may be assigned to molecules which are analogous to those for atoms. NO has a ^2P ground state, the separation of the components being about $.6kT$ at ordinary temperatures. Van Vleck* has given a detailed calculation which leads to a magneton value agreeing to within 1.5 per cent. with that observed. The magneton value, however, should vary with the temperature, and it would be of great interest if the susceptibility could be examined over a sufficient range to test this conclusion.

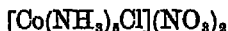
The electrons in N_2 (14) form a closed configuration. The ^2P state of NO (15) is what would be anticipated from the addition of one p electron. The spectrum of O_2 (16) has not yet been fully analysed. A diamagnetic $^1\text{S}_0$ ground state would be anticipated as the lowest

* J. H. Van Vleck, *Phys. Rev.*, 31, 587 (1928).

due to two p electrons; in this state the electron spins balance out. The susceptibility, however, agrees with that for a 3S_1 state—corresponding to 2 Bohr magnetons—the moment being entirely due to the two parallel electron spins. This is very surprising, and the question as to why oxygen is paramagnetic remains at present completely unsolved.*

COMPLEX SALTS †

The investigation of the magnetic properties of certain complex salts is of great interest when the results are considered in connexion with theories as to their structure. As classical examples of complex salts the cobaltammines may be considered. With the Werner symbolism, a typical cobaltamine may be represented by the formula



The compound ionizes as indicated by the bracket, giving a complex ion $[\text{Co}(\text{NH}_3)_6\text{Cl}]^{++}$. Although the simple Co^{++} ion is paramagnetic, the complex ion is diamagnetic. If Sidgwick's interpretation of the structure is adopted, it is possible to calculate the number of electrons, giving the 'effective atomic number' z , associated with the central atom in the complex. Each $(\text{NO}_3)^-$ group outside the bracket, removes 1 electron; inside the bracket the Cl adds 1 electron (by sharing) and each NH_3 adds 2 (one by transfer and one by sharing). The effective atomic number is therefore given by

$$z = 27 - 2 + 1 + (5 \times 2) = 36$$

The number of electrons associated with the central atom is thus the same as the number in the inert gas

* E. C. Stoner, *Phil. Mag.*, 3, 336 (1927).

† For results see E. Rosenbohm, *Zeits. für Phys. Chem.*, 93, 693 (1919); L. A. Welo, *Phil. Mag.*, 6, 481 (1928); for discussion, L. C. Jackson, *Phil. Mag.*, 2, 86 (1926); 4, 1070 (1927); D. M. Bose, *Phil. Mag.*, 5, 1048 (1928); E. C. Stoner, *Proc. Leeds Phil. Soc.*, 1, 226 (1928).

atom krypton, and presumably forms a closed configuration of the same type, with a zero magnetic moment. All the cobaltamines are diamagnetic for the same reason—that the number of electrons associated with the central atom, 36, is such as to form a closed configuration. This is found also for salts of the potassium ferrocyanide type.

When the effective atomic number is not equal to that of a closed configuration, the complex ion may be paramagnetic. In the following table are given the approximate magnetic moments (p values) found for ions of a number of complex salts, Z being the atomic number, and z the effective atomic number of the central atom.

TABLE X.

Moments of Complex Ions of Elements of First Transition Series.

	Fe	Cr	Co	Ni	Cu	Fe	Fe	Co		Ni
Z	26	23	27	28	29	26	26	27		28
z	32	33	33	34	35		36		37	38
p	24	19	23	13	9	10	0	0		16

The moments found are of the same order of magnitude as those for atoms in S states (Table VII), but there is difficulty in giving a precise interpretation of the results. It is not known how the electrons associated with the central atom are distributed among the possible quantum states, and the magnetic data available are not at present sufficiently numerous or precise to distinguish between the various possibilities. To take a particular example, the 33 configuration may contain a closed group of 30 electrons, and 3 p electrons in the

$n = 4$ level, giving a ${}^4S_{3/2}$ state ($p = 19.3$); or of a closed group of 18, an incomplete group of 7 d electrons in the $n = 3$ level, and a closed group of 8 for which $n = 4$. This would give rise to a ${}^4F_{1/2}$ state for which, on the view previously developed, p may have a value ranging from 19.3 to 25.8 (see Table VIII). More extended magnetic measurements promise to throw considerable light on the distribution of electrons in these complex ions.

It is of interest to note that the amines of Ru, Rh and Pd are diamagnetic when the effective atomic number is equal to the atomic number of the inert gas xenon (54); and those of Os, Ir and Pt for an effective atomic number 86 (emanation). Further investigations both of the simple and complex ions of transition series of elements other than the first are most desirable.

At present the general manner in which the magnetic properties of complex ions are to be interpreted is fairly clear, but many details are obscure; and much more experimental work will be necessary before the whole problem can be satisfactorily surveyed.

CHAPTER IV

FERROMAGNETISM

IRON and other ferromagnetics are qualitatively distinguished magnetically from other substances by the fact that they may acquire a relatively high magnetization in weak fields. (In a field of 10 gauss, for example, the specific intensity of magnetization of antimony, a diamagnetic, is about -0.8×10^{-6} , and of cobalt sulphate, a paramagnetic, about 0.6×10^{-3} , while that of a typical specimen of soft iron is about 200.) In general for ferromagnetics there is not a linear relation between the magnetization and the field strength. The susceptibility, defined formally as the ratio of the intensity of magnetization to the field strength, therefore varies with the field, so that the magnetic characteristics of a ferromagnetic cannot be specified in so simple a manner as can those of dia- and paramagnetics. The magnetization, moreover, is not a unique function of the field strength, but depends also on the fields to which the specimen has previously been subjected. If the field is varied cyclically, the well-known hysteresis curve is traced out. Of particular importance is the fact that a ferromagnetic may exist in a permanently magnetized state when there is no external field. Above a certain critical temperature, however, all ferromagnetics become paramagnetic; and when it is stated that a substance is ferromagnetic it is to be understood that this refers to a range of temperatures below the critical temperature, that is, below the Curie point. Ferromagnetics exhibit a very wide range of phenomena which have been extensively investigated not only owing to their intrinsic scientific interest, but also on

account of their technological importance. It may be said that at present there is no theory which accounts in a completely satisfactory manner for even the more salient characteristics of ferromagnetics ; but the treatment of Weiss, supplemented by the quantum theory, does introduce order into chaos, and serves to correlate many of the facts. In the theory of Weiss the molecular field plays an important rôle, and it is only since the advent of the new quantum mechanics that there has been even the beginning of a satisfactory explanation of the origin of this mysterious field. In the following account of ferromagnetism, Weiss's theory will first be described, together with the modifications suggested by classical quantum theory. Some of the more important facts will then be reviewed, roughly in the order of ease of theoretical interpretation. Finally a brief indication will be given of the mode of attack on the molecular field problem suggested by recent developments in quantum mechanics.

THEORY

Weiss's theory of ferromagnetism is made up of two essentially distinct parts. In the first, the general theory which applies to paramagnetism is developed for the case where the temperature is below the Curie point. The ideal characteristics theoretically deduced do not agree with those observed experimentally for ferromagnetics in bulk, and it must be assumed that the treatment applies directly only to small 'domains' of the order of magnitude usually found for microcrystals, but not necessarily to be identified with them. The second part of the theory deals with the relation of the ideal properties of these domains to the bulk properties usually observed.

For the ideal ferromagnetic domains exactly the same assumption is made as for paramagnetics, namely that in addition to the external field H , there is an internal 'molecular field' proportional to the intensity of mag-

netization, so that for the effective resultant field, H_e

$$H_e = H + NI \quad . \quad . \quad . \quad . \quad (1)$$

Let $a = \mu H_e / kT$. The case where a is small has been previously discussed (Chapter III, Equations 8-10). When the molecular field coefficient N is positive, the possibility arises of spontaneous magnetization in the absence of an external field. Consider a gram molecule of the substance of molecular weight m and density ρ .

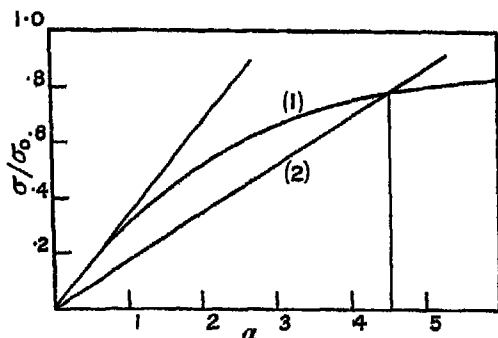


FIG. 9.—(1) $\sigma/\sigma_0 = \coth a - 1/a$
(2) $\sigma/\sigma_0 = (mRT/N\rho\sigma_0^2)a$

Let σ be the gram molecular magnetic moment, σ_0 the saturation moment. As before (III, 2)

$$\frac{\sigma}{\sigma_0} = \coth a - \frac{1}{a} \quad . \quad . \quad . \quad . \quad (2)$$

When the external field is zero

$$a = \frac{\mu NI}{kT} = \frac{\sigma_0 N \rho \sigma}{RT m}$$

$$\frac{\sigma}{\sigma_0} = \frac{mRT}{N\rho\sigma_0^2} a \quad . \quad . \quad . \quad . \quad (3)$$

The state of magnetization is determined by the simultaneous equations (2) and (3), the content of which

is most readily seen from their graphs. Equation (2) gives the Langevin curve, and (3) a straight line through the origin, whose slope increases with T .

At the origin the slope of the tangent to the Langevin curve is $1/3$; there will be a non-zero point of intersection when the slope of the straight line is less than that of this tangent, that is when

$$\frac{mRT}{N\varrho\sigma_0^2} < \frac{1}{3}$$

$$T < \frac{N\varrho\sigma_0^2}{3mR} \quad . \quad . \quad . \quad . \quad (4)$$

$$T < \theta$$

It may readily be shown that the point of intersection at the origin corresponds to an unstable state. When T is less than θ (where θ has the same significance as for paramagnetics—see III, 10), the second point of intersection corresponds to a stable state of spontaneous magnetization. As the temperature decreases the intensity approaches the true saturation intensity.

Equation (3) may be written

$$\frac{\sigma}{\sigma_0} = \frac{T}{\theta} \cdot \frac{\alpha}{3} \quad . \quad . \quad . \quad . \quad (3a)$$

α may be eliminated between (3a) and (2) giving

$$\frac{\sigma}{\sigma_0} = f\left(\frac{T}{\theta}\right) \quad . \quad . \quad . \quad . \quad (5)$$

where $f\left(\frac{T}{\theta}\right)$ approaches 1 as T approaches 0; and 0

as T approaches θ . The graph of $f\left(\frac{T}{\theta}\right)$ is shown in

Fig. 10, and also the observed curve for nickel. While the general trend of the two curves is the same, the difference between them is considerable.

Ideally a substance containing 'carriers' (molecules, atoms or ions) with a permanent magnetic moment, and having a positive molecular field constant, will behave as a paramagnetic above a certain critical temperature θ , and will follow the Weiss law $\chi = C/(T - \theta)$. The elementary magnetic moment may be determined from the variation of the susceptibility with temperature,

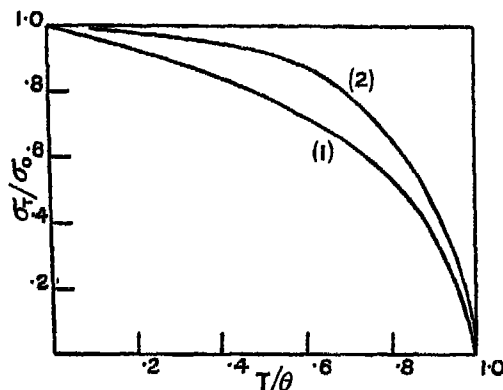


FIG. 10.— σ/σ_0 as a function of T/θ

(1) Theoretical.

(2) Observed for Nickel.

and the molecular field constant from the magnetic moment and the critical temperature. Below the critical temperature, in the absence of an external magnetic field it will be spontaneously magnetized to a degree depending on the temperature, approaching the saturation value as the temperature approaches absolute zero. Weiss supposes that an ordinary ferromagnetic is built up of domains which are spontaneously magnetized in this way. The direction of magnetization of each domain is indeterminate, and if the directions are distributed at random, the substance as a whole will appear unmagnetized. External fields which

can be applied will in general be small compared with the molecular fields and their main effect will be in altering the direction of the spontaneous magnetization without appreciably changing its magnitude. When an external field is applied each domain may be supposed to behave in a manner analogous to that of an elementary crystal of pyrrhotite.

Pyrrhotite is a ferromagnetic crystal which occurs in the form of hexagonal prisms of approximate composition FeS . The phenomena observed with an ordinary crystal are somewhat complicated, but Weiss has shown that they may be readily explained by supposing each crystal to be composed of associated elementary crystals, the behaviour of which is particularly simple. These elementary crystals have a 'magnetic plane' (parallel to the base of the prism) in which there is an axis of easy magnetization. The crystal is normally spontaneously magnetized along this axis, and application of an external field (provided it is not very large) in the direction of magnetization does not increase the intensity. If a gradually increasing field is applied in the opposite direction, there is no change until the coercive field (about 15 gauss) is passed, when the intensity of magnetization changes in sign but not in magnitude. The hysteresis curves are thus simple rectangles, saturation (in the ordinary sense) being attained in a field of about 15 gauss. At right angles to this direction in the magnetic plane fields of about 7,300 gauss are required for saturation; while at right angles to the plane fields of about 150,000 gauss would be necessary.

If an ordinary ferromagnetic consists of domains with the directions of spontaneous magnetization arranged at random, and behaving somewhat similarly to the elementary crystals of pyrrhotite, the ordinarily observed effect of applying an external field will be qualitatively explained. The successive stages are represented by the following figure, in which the arrows represent the direction of magnetization of the domains.

Let H_c be the coercive field for a domain. The direction of magnetization of a domain with a resolved moment opposed to the field will change sign when the resolved field is equal to H_c , that is when H is equal to $H_c/\cos \theta$. At first the external field will have little effect, the first changes in sign occurring when $H = H_c$. More and more domains will then reverse their direction of magnetization, this corresponding to the steep irreversible part of a hysteresis curve. Finally there will be a reversible increase in magnetization due to the

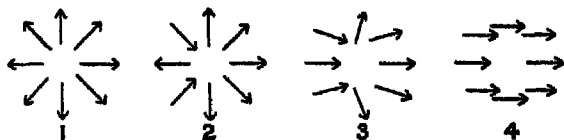


FIG. 11.—Illustrative of the Process of Magnetization of a Ferromagnetic according to the 'domain' theory

The arrows represent the distribution of the directions of magnetization of the domains. The figures 1 to 4 show the successive stages from the unmagnetized to the saturated state.

direction of magnetization of each domain tends towards that of the external field—the actual intensity of magnetization then being that appropriate to the temperature and the resultant of the external and the molecular field. The magnitude of the coercive field may vary for different domains, and the theory has to be left in a qualitative form. As far as it goes, however, it is of great value, for it provides a fairly simple general scheme which correlates a large number of diverse detailed facts. The shortcomings of the theory, and the modifications necessary, are best considered in connexion with the detailed experimental facts.

THE GYROMAGNETIC EFFECT

On any theory which attributes magnetic moment to the orbital motion of electrons, magnetization should be accompanied by a change in angular momentum.

This was pointed out by O. W. Richardson in 1908. The relation between the magnetic moment μ and the mechanical moment j of an orbital electron is

$$\mu = \frac{e}{2mc}j \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For a magnetic 'carrier' generally, let R be the ratio of j to μ ; so that for an orbital electron

$$R = j/\mu = 2mc/e = -1.13 \times 10^{-7} \quad . \quad . \quad (7)$$

When a rod is magnetized, so that its magnetic moment is M , it will acquire an angular moment J due to reaction (since no couple is applied to it) such that

$$J = -RM$$

Since R is small, tests of this relation have hitherto been confined to ferromagnetics, for which M may be large. Even for ferromagnetics the experiment is difficult, since great care has to be taken to eliminate secondary effects which may be much larger than the effect which is being investigated. In the most direct method, the rod is suspended in a helix, and the angular momentum acquired on magnetization deduced from the throw and the torsional constant of the suspending fibre. Other less direct methods, in which the resonance effect with alternating magnetization is utilized, have been successfully applied. For all the substances investigated—iron in various forms, nickel, cobalt, magnetite, and Heusler alloys—it has been found that within the limits of experimental error the ratio of the mechanical to the magnetic moment is half that to be anticipated if the magnetism was due to orbital electrons. The converse experiments, in which the magnetization due to the rotation of a rod is measured, give the same results.

$$R_{exp} = mc/e \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$$\text{or} \quad \mu/j = 2(e/2mc) \quad . \quad . \quad . \quad . \quad (9a)$$

Now μ/j expressed in terms of $e/2mc$ is equal to g , the splitting factor of spectroscopic theory (Chapter I,

Equations 7, 8). The experiments therefore indicate that the value of g for the magnetic carriers in ferromagnetics is 2; and so suggest that the magnetization of ferromagnetics is entirely due to the intrinsic spin of the electrons. It was seen in connexion with ionic paramagnetism that there is considerable support for the view that the orbital moment, though present, may not be fully effective, so that from the gyromagnetic effect experiments it cannot be concluded that it is the 'free' electrons which are responsible for the magnetism, but rather that only the spin moment of the electrons (in atoms or ions) is magnetically effective. This question will be further discussed in the next section.

THE ATOMIC MOMENTS OF FERROMAGNETICS *

The intensity of magnetization of an ordinary paramagnetic approaches the saturation value only at very low temperatures and in very high fields. A ferromagnetic may be said to provide its own field, the effect of which is rendered apparent by the application of a relatively small external field. As the external field is increased from zero, the specimen being initially unmagnetized, the intensity increases at first slowly and then rapidly; finally it reaches a stage in which it increases very slowly and linearly with the field. Extrapolation to zero field gives the value of the spontaneous magnetization appropriate to the temperature. Some examples of the curves for nickel at different temperatures are shown in Fig. 12.

By carrying out experiments at low temperatures an estimate can be made of the spontaneous magnetization at absolute zero (see Fig. 10), this giving the saturation intensity in the Langevin sense. This corresponds to parallelism of the magnetic carriers. Assuming these to be atoms, the gram atomic magnetic moment σ_a may be deduced directly from the saturation intensity I_s . Let ρ be the density, A the atomic weight

* E. O. Stoner, *Proc. Leeds Phil. Soc.*, 1, 55 (1926).

$$\sigma_A = \frac{I_0 A}{e} \quad . \quad . \quad . \quad . \quad . \quad (10)$$

The Weiss magneton value per atom is given by

$$p = \frac{\sigma_A}{1123.5} \quad . \quad . \quad . \quad . \quad . \quad (11)$$

At temperatures above the Curie point, the Weiss

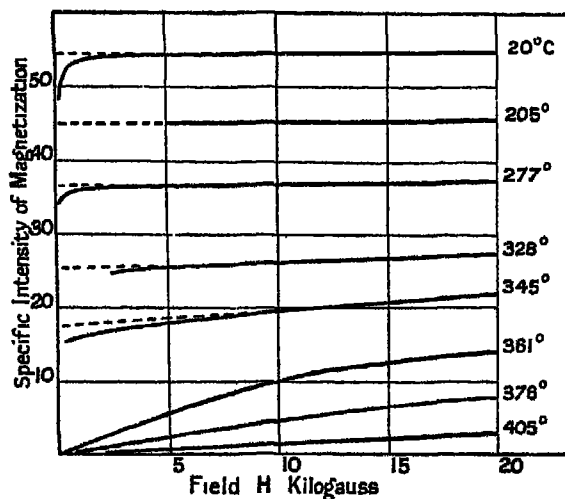


FIG. 12.—Magnetic Isothermals of Nickel

magneton value may be deduced in the usual way from the slope of the $1/\chi$, T curve.

$$p = \frac{\sqrt{3RC_A}}{1123.5} = 14.07\sqrt{C_A} \quad . \quad . \quad . \quad (12)$$

At low temperatures the three ferromagnetic elements and their binary alloys have been investigated. The results for the magnetic moment per atom are shown in Fig. 13.

At the singular points in the curves the composition corresponds to a simple ratio in the number of atoms.

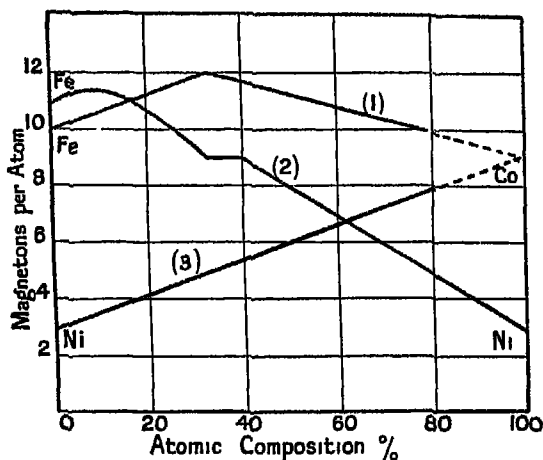


FIG. 13.—Magnetic Moment per Atom in Ferromagnetic Alloys, from Low Temperature Saturation Intensity
(1) Fe — Co. (2) Fe — Ni. (3) Ni — Co

The variation of $1/\chi$ with T above the Curie point is indicated in Fig. 14.

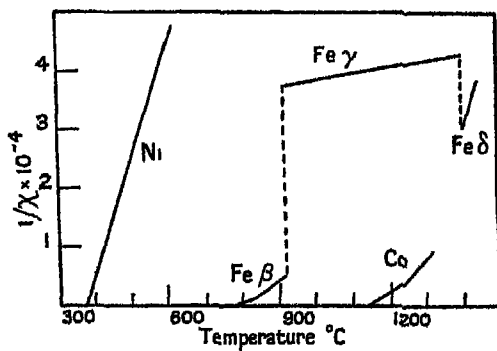


FIG. 14.—Variation with Temperature of Susceptibilities of Ferromagnetic Elements above the Curie Point

The sudden discontinuities in the curve for iron are particularly noteworthy. It may be noted that γ iron has a face centred crystal structure, while β iron has the same body centred structure as α iron (below the Curie point). On the Weiss theory there is not necessarily any change in the structure on passing through the Curie point, although there is a change in the magnetic properties. The values of the magnetic moments per atom calculated from the variation of susceptibility over different temperature ranges are shown in the following table, and also the value of θ in the expression $\chi = C/(T - \theta)$.

TABLE XI.

Magnetic Constants of Iron, Cobalt and Nickel above the Curie Point.

	Temperature Range. ° C.	θ	p
Fe β_1	774-828	1047	20.9
	828-920	1063	17.4
	920-1395	-1340	28.2
	1395-	1543	7.05
Co β_1	1170-1241	1404	15.9
	1241-1303	1422	14.55
Ni β_1	412-900	645	8.02
	900-	—	8.96

By a comparison of Table XI and Fig. 13 it will be seen at once that there is no agreement between the p values deduced from measurements on the saturation intensity at low temperatures and on the paramagnetic susceptibility at high. This might be attributed to a change in structure, but although this does occur in some cases (as in the change from β to γ iron) there is no evi-

dence of a general change of structure in passing through the Curie point (as from α to β iron).

There are two directions in which the theory requires modification. The treatment has been made on a classical basis, and the assumption has been made that the same magnetic moment is associated with each atom. Now the results on alloys (Fig. 12) suggest very strongly that the magnetic properties are determined by groups of atoms. The groups do not necessarily play a primary part in determining the crystal structure, but contain the minimum number of atoms which, by interchange, sharing or loss of electrons, can give rise to the same mean magnetic moment per atom as that observed for the material as a whole.

Let there be n atoms in a group, and let $p_1, p_2 \dots p_i \dots p_n$ be the magnetic moments associated with the atoms. Let p_i be the mean moment per atom deduced from the saturation intensity, p_r that deduced from the paramagnetic susceptibility; then p_i is an arithmetic mean (since the magnetic moments are parallel to each other) while p_r is a root mean square value (as can be seen from Equations 4, 5 and 12 of Chapter III).

$$p_i = \frac{1}{n} \sum p_i \dots \dots \dots (13)$$

$$p_r = \sqrt{\sum p_i^2 / n} \dots \dots \dots (14)$$

Though the values of the magnetic moments associated with each atom may remain constant, the mean values deduced from the saturation and paramagnetic measurements may be entirely different.

As an example the case of nickel may be considered, for which $p_i \doteq 3$, $p_r \doteq 8$. The magnetic singularity of the iron nickel alloy of composition Fe_3Ni_2 (Fig. 13) suggests that a group of five atoms may be concerned. Since saturation corresponds to the alignment of the elementary moments parallel to the field the resolved moments must then be integral multiples of the Bohr

unit, or approximately, integral multiples of 5 Weiss units. If it is assumed that in every group of five nickel atoms there are three with zero moment, one with one Bohr magneton and one with two, the observed value of p will be obtained.

$$p_s = \frac{1}{5}\{(3 \times 0) + (1 \times 5) + (1 \times 10)\} = 3 \quad (13a)$$

At low temperatures in a solid it is probable that only the electronic spin moment is effective. The nickel atom, with 28 electrons, will normally form a closed diamagnetic configuration; the Ni^+ ion with 1 electron less, has a magnetic moment of 1 Bohr unit, and the Ni^{++} ion of 2 units. Thus the assumption that in a group of 5 atoms ionization occurs to give 3 Ni, 1 Ni^+ and 1 Ni^{++} will account for the low temperature results. Other groups might, of course, be chosen to give the same mean magnetic moment, but the value of the general idea lies in the possibility of accounting for the high temperature paramagnetic susceptibility with the same group.

At high temperatures the orbital moments may become partially effective, and the magnetic moments associated with Ni^{++} , Ni^+ and Ni will be approximately the same as those deduced from measurements on paramagnetics for ions with 26, 27 and 28 electrons (see Table VIII, Chapter III) namely 16, 9 and 0. The value of p_p may be calculated from (14)

$$p = \sqrt{(16^2 + 9^2)/5} = 8.2 \quad . \quad . \quad (14a)$$

This value is in reasonably good agreement with that observed (8.0).

For nickel, therefore, the entirely different magnetic moments per atom deduced from the saturation intensity below the Curie point, and from the paramagnetic susceptibility above may be accounted for without the necessity for supposing that there is any change in the number and nature of the elementary carriers present. By making appropriate (and reasonable) assumptions as to the ionization within groups of atoms, the dis-

crepancies between the observed low and high temperature moments (indicated by Fig. 12 and Table XI) can all be accounted for in a similar way.

It has been seen before that the observed curve for the variation of the saturation intensity of nickel with temperature diverges considerably from that predicted by the classical treatment (Fig. 10). It may be noted here that the appropriate quantum modification, consistent with the above assumptions, gives a very much better agreement.

On the present view ferromagnetism is to be attributed to the spin moments of the electrons in the atoms and ions, and not to the spin moments of free electrons, which normally should give rise only to a small paramagnetism (Chapter V). That only the spin moments of electrons are effective at low temperatures is consistent with the observed gyromagnetic effect, and that these electrons are not free is in agreement with the Heisenberg treatment of ferromagnetism which will be considered later.

MAGNETO-THERMAL EFFECTS

In the neighbourhood of the Curie point there is a rapid variation with temperature in the specific heat of iron and other ferromagnetics. Below the Curie point, according to the Weiss theory, a ferromagnetic is spontaneously magnetized although the magnetization may not be apparent for the material in bulk. As the temperature changes, there will be a change in the magnetic energy, and a part S_M of the specific heat arises from this. Let U_M be the magnetic energy per unit mass, H , the molecular field.

$$U_M = -\frac{1}{\rho} \int H_s dI = -\frac{1}{\rho} \int NI dI = -\frac{1}{2} \frac{NI^2}{\rho} \quad (15)$$

The part of the specific heat due to the change in magnetic energy is therefore given by

$$S_M = \frac{dU_M}{dT} = -\frac{1}{2} \frac{N}{\rho} \frac{dI^2}{dT} \quad . \quad . \quad (16)$$

Above the Curie point there is no spontaneous magnetization, so that U_M is zero; as the Curie point is approached from below, the spontaneous magnetization decreases more and more rapidly, so that the specific heat should rise to a maximum and then fall off suddenly to the normal value.

The change in the specific heat of nickel at the Curie point has been measured by Weiss. It is in qualitative agreement with that calculated from the change in the magnetization. For manganese arsenide (a ferromagnetic with the low Curie temperature of about 45°C.), Bates * has found that the specific heat rises to a maximum and falls off to a steady value within a few degrees. Careful experiments by Sucksmith and Potter,† however, have shown that the change is not always so sudden as that indicated by the theory. For nickel the decrease is spread over about 25° in the neighbourhood of the Curie point. The reason for the incomplete agreement between theory and experiment is not yet clear, though the theory of spontaneous magnetization undoubtedly provides an explanation of the main effects observed.

A further confirmation of the theory of spontaneous magnetization is afforded by the magneto-caloric effect, discovered by Weiss. When a strong magnetic field is applied to a ferromagnetic, magnetization is accompanied by a reversible change of temperature. This is not to be confused with the temperature change associated with hysteresis, which is irreversible. Further, while the temperature change accompanying a hysteresis cycle usually does not exceed a few thousandths of a degree, the magneto-caloric change may be of the order of one degree. Let ΔT be the change of temperature due to a change ΔH in the field. By simple thermodynamical reasoning it may be shown that

$$\Delta T = - \frac{T}{S} \frac{1}{g} \frac{dI}{dT} \Delta H (17)$$

* L. F. Bates, *Proc. Roy. Soc.*, 117, 680 (1928).

† W. Sucksmith and H. H. Potter, *Proc. Roy. Soc.*, 112, 157 (1926).

The change in temperature should be greatest at the Curie point, where dI/dT is greatest; this is actually found. From the equation the specific heat, S , may be calculated from the magneto caloric data (giving $\Delta T/\Delta H$) and purely magnetic data (giving dI/dT). The specific heat so calculated agrees remarkably well with that determined directly (Fig. 15).

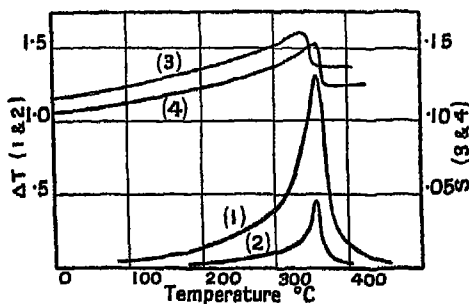


FIG. 15.—Curves 1 and 2. Magneto-caloric Effect in Nickel
 1. $\Delta H = 17,775$ gauss.
 2. $\Delta H = 4,160$ gauss.
 Curves 3 and 4. Specific Heat of Nickel.
 3. From magneto caloric effect.
 4. Calorimetrically.

It is only the true increase in magnetization which is accompanied by the magneto-caloric temperature change, and not that due to the change of the direction of magnetization in the elementary domains. When the intensity of magnetization produced is not too small, the temperature change increases linearly with the square of the intensity.

$$\Delta T = A(I^2 - I_0^2) \quad \dots \quad (18)$$

The constant I_0 in this equation represents the spontaneous intensity of magnetization. Measurements on the magneto-caloric effect at various temperatures therefore enable the values of spontaneous intensity to be

deduced. The values agree well with those deduced by extrapolation to zero field of the linear parts of the ordinary magnetization curves obtained in strong fields.

The actual magnitude of the decrease in the specific heat at the Curie temperature presents some points of interest. Let A be the atomic weight of the substance, n the number of independent magnetic carriers associated with each atom. Then on a classical basis (that is assuming that any orientation of the magnetic axes of the carriers is possible) it may be shown that approximately

$$\Delta S = -\frac{5nR}{2A} \quad . \quad . \quad . \quad (19)$$

If it is assumed that the ferromagnetism is due to electron spin, so that the carriers must be parallel or anti-parallel to the field

$$\Delta S = -\frac{3n'R}{2A} \quad . \quad . \quad . \quad (19a)$$

In this case n' will give the number of electrons per atom which contribute to the magnetism. The data* are given in the following table.

TABLE XII
Specific Heat Change at the Curie Point.

	ΔS Calories per degree per gram.	$A \Delta S$ Calories per degree per gram atom.	n .	n' .
Nickel0285	1.7	.34	.57
Iron122	6.8	1.36	2.27

In the last section it was shown that the magnetic properties of nickel were in agreement with the view that there were 3 effective electrons in 5 atoms, giving $n' = .6$; for iron 7 effective electrons in 3 atoms are required, giving $n' = 2.33$. These values agree well with those deduced from the specific heat change,

* See R. H. Fowler and P. Kapitza, *Proc. Roy. Soc.*, 124, 1 (1929).

MAGNETISM

g that it is electron spin which is responsible for ferromagnetism.

experiments have recently been made on the variation with temperature of the thermo-electric motive force developed in a circuit containing iron and a non-ferromagnetic metal.* From the results in passing through the Curie point, the change in specific heat of the electrons has been estimated. A conclusion is drawn † that the whole change in specific heat at the Curie point is to be attributed to the electrons, and not to the ions or atoms. The word 'free' is a somewhat indefinite term, the essential point may be put more satisfactorily in the form that the electrons responsible for the magnetic effects are the same as those responsible for the conductivity. The line of attack on the problem is a most interesting one, but the conclusion raises many difficulties, and more experiments can be accepted further experiments and a more thorough theoretical treatment are necessary.

MAGNETIZATION WITH FIELD

Attention has been mainly directed to the study of ferromagnetics connected with the spontaneous magnetization, of which a rough measure is given by the saturation intensity in relatively strong fields. The behaviour of ferromagnetics in relatively weak fields is of great technical importance, but as this is a familiar only a brief general account will be given.

The manner in which the magnetization varies with the applied field for a typical specimen of steel is shown in Fig. 1.

As a gradually increasing field is applied to an unmagnetized specimen, the magnetization first increases slowly (AB) and then more rapidly (BC), and finally approaches the saturation value (CD).

* Jaannus and R. Jaannus, *Zeits. für Phys.*, 54, 277 (1929).
† Jaannus and I. Kikoin, *Zeits. für Phys.*, 54, 289 (1929).

For the initial part of the curve the susceptibility is approximately given by

$$\kappa = \frac{I}{H} = \kappa_0 + bH \quad . \quad . \quad . \quad (20)$$

κ_0 being the 'initial susceptibility' and b a constant. The initial permeability $\mu_0(\mu_0 = 1 + 4\pi\kappa_0)$ varies from about 40 for hard steels to as much as 8,000 for some iron-nickel alloys. The permeability rises in the steep

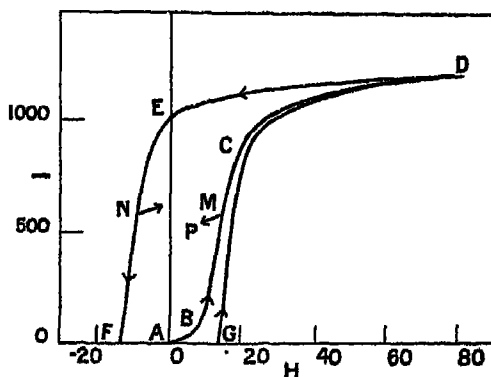


FIG. 16.—Variation of Magnetization with Field

part of the curve to a maximum and then decreases. The maximum permeability for a number of substances is given in Table XIII (p. 83). Approximate saturation is reached in lower fields the higher the initial susceptibility.

When the field is gradually reduced the magnetization follows the path DEF. If the field is varied cyclically between limits $+H$ and $-H$, a hysteresis curve is traced out, of which the upper part is shown in Fig. 16 (GDEF). If the limiting field is sufficient to saturate the specimen, the residual magnetization when the field is reduced to zero is known as the remanence, and is specified by the remanent intensity I_r , or induction

$B_r(B_r = 4\pi I_r)$ —corresponding to OE in the figure. The reverse field required to reduce the magnetization to zero (OF) is known as the coercivity, H_c .

The complicated character of the magnetization curves of ferromagnetics is due to the occurrence of both 'reversible' and 'irreversible' changes in the process of magnetization. On the theory which has been given, in an irreversible change the direction of magnetization in a spontaneously magnetized domain turns suddenly through a large angle (possibly two right angles). In a reversible change it turns gradually, as the field increases, towards the direction of the field, taking up an equilibrium direction under the influence of the external field and that arising from surrounding domains. The intensity of magnetization also increases slightly, as the effect of the external field is added to that of the molecular field.

To a certain extent the two processes may be separated. If the field is decreased by a small amount δH when the specimen has reached the state represented by M the path MB is not retraced, but the intensity decreases by an amount δI represented by the short line MP. This change is reversible, for the path PM is retraced on increasing the field again. Similar reversible changes occur on increasing the field slightly at N. The ratio $\delta I/\delta H$ under these conditions is known as the reversible susceptibility κ_r , and it is found to depend only on the intensity of magnetization (being, for example, the same at M and N). The reversible susceptibility is a maximum when the specimen is unmagnetized (being then equal to κ_0) and falls off towards zero as saturation is approached. The curve relating κ_r/κ_0 to I/I_∞ (I_∞ being the saturation intensity) is approximately the same for different ferromagnetics.

The irreversible changes occur mainly on the steep part of the magnetization curve. If the field is increased continuously, the magnetization may increase discontinuously, the magnitude of the discontinuities pre-

sumably depending on the size of the domains through which sudden changes occur in the direction of magnetization. Such discontinuities were first demonstrated by Barkhausen (1919), who used a device by which the sudden changes in magnetization were made audible. They were later investigated more directly by Forrer,* using a quick-acting magnetometer. He showed that for a specially treated nickel wire the magnitude of a discontinuity might reach a considerable fraction of the maximum magnetization. Estimates may obviously be made of the size of the domains throughout which these discontinuous changes occur, but up to the present no correlation has been found between the size of the domains, and the size of the crystalline 'grains' of the material. The whole subject is one which promises to repay more extensive investigation.

The area enclosed by a complete hysteresis curve gives a measure of the work done in carrying a cubic centimetre of the specimen through the corresponding magnetic cycle.

$$W = \int H dI = \frac{1}{4\pi} \int H dB \quad . \quad . \quad . \quad (21)$$

This work is converted into heat, and is known as the 'hysteresis loss', which is greater the greater the maximum induction; the relation being given with fair approximation by a formula due to Steinmetz

$$W = \eta B^{1.6} \quad . \quad . \quad . \quad . \quad (22)$$

Although the rise in temperature due to taking a specimen through a single cycle may be small, it would become considerable when continuous rapidly alternating fields were applied; so that, for the material of transformer cores, for example, it is necessary that the hysteresis loss should be as small as possible. The losses for a number of materials are shown below. In addition to the hysteresis loss, there is also a loss due to eddy currents. The particular suitability of silicon

* R. Forrer, *Journ. de Phys.*, 7, 109 (1926).

steel for transformer cores lies in the fact that not only is its hysteresis loss small, but also its specific resistance is relatively high, so that the eddy current loss is greatly diminished. It is of interest to note that the Steinmetz formula (22), though of general application as an approximation, is purely empirical. In fact, no satisfactory quantitative theoretical treatment of hysteresis seems yet to have been given.

For a material to be suitable for strong permanent magnets it is not sufficient that the true remanence (determined by a ring method) should be large. A specimen in the form of a bar or a horse-shoe is subject to the demagnetizing field due to the poles at its ends, and it is necessary that the intensity of magnetization under the influence of this field—the apparent remanence—should be as large as possible. A consideration of the shape of the hysteresis curve will show that the apparent remanence will approach the true remanence more nearly the greater the coercivity. A good approximate measure of the effectiveness of materials for magnets is given by the product of H_c and B_r , so that materials in which the hysteresis loss is small will be quite unsuitable. Since high remanence is usually associated with low coercivity, the production of materials in which both remanence and coercivity are high has presented a most interesting technical problem. High carbon steels have been much used and also tungsten steels. For short magnets the cobalt steels form the most suitable material, some of them having a coercivity of as much as 240 gauss.

Some of the characteristics of a number of materials are shown in the following table. The maximum intensity of magnetization depends on the chemical composition, but the other values depend greatly on the details of the thermal and mechanical treatment, and must be regarded as typical rather than exact. For technical applications it must be remembered that the cost of production is one of the controlling factors which has to be considered.

TABLE XIII.

Magnetic Constants of Some Ferromagnetic Materials.
 W. Hysteresis loss. Ergs per c.c. for $B_{max} = 10,000$.

	$4\pi I_{max}$	B_r	H_c	W	$\frac{H_c}{B_r} \times 10^{-4}$	μ_{max}
Electrolytic Iron . .	21,600	10,850	0.37	810	0.4	—
Dynamo Steel . . .	21,420	11,050	0.37	1,400	0.4	14,800
Cast Iron	16,420	5,100	11.4	30,000	5.8	240
Carbon Steel (1% C) .	18,400	7,000	60	—	42	—
Tungsten Steel (1% C, 5% W)	—	10,400	62	—	65	—
Cobalt Steel (36% Co) .	—	9,310	227	—	211	—
Silicon Steel (4% Si) .	19,700	7,830	.47	1,600	0.4	7,500
Nickel	6,400	3,340	1.6	—	0.5	1,120
Cobalt	17,700	3,100	12	—	3.6	175
Ferronickel (78% Ni) (Permalloy)	10,500	5,500	.05	200	0.08	74,000
Ferrocobalt Fe_3Co . .	23,680	8,230	2.7	—	2.2	—
Heusler Alloy (61% Cu, 24% Mn 15% Al) . .	4,100	2,550	7.3	—	1.8	—

It would be out of place here to attempt any detailed discussion of the magnetic properties of the various materials, and of the way they are affected by particular treatments, for which the technical literature must be consulted. The general term 'iron' is used not only for the pure metal, but also for commercial iron which may contain a large amount of impurities. The magnetic and other properties are greatly affected by even small amounts of impurities, and on the manner in which they are associated with the iron, depending on the mode of manufacture and on the subsequent treatment. The effect of varying quantities of carbon, in particular, has been investigated in great detail. Researches on the effects of additions of silicon, manganese, tungsten, chromium have led to the introduction of new steels of great technological value. Investigations on the binary alloys have led to the discovery of ferrocobalt, the saturation intensity of which is greater than that of either of its constituents, making it most

suitable for the pole pieces of powerful electromagnets ; and of the remarkable ferronickel permalloy, which is almost saturated in the earth's magnetic field, and has an enormously high initial permeability, making it most suitable for the loading of cables.

That ferromagnetic alloys can be formed from non-ferromagnetic constituents was discovered by Heusler in 1898, and since then these alloys have been extensively investigated. Some of the binary alloys of manganese are ferromagnetic. In the ternary alloys manganese and copper seem to be essential, while a number of elements may be used as the third constituent. Aluminium gives the most magnetizable alloys, the saturation intensity being a maximum for about 13 per cent. Al. Heusler has suggested that the carrier of the ferromagnetism is a group of atoms $Al_x(Cu, Mn)_x$ —with one atom of Al to three of Cu and Mn together. Manganese and copper are neighbours of the ferromagnetic elements, and it seems probable that in this group of atoms electronic configurations similar to those in the ferromagnetic metals are reproduced.

SINGLE CRYSTALS

Recent improvements in the technique for the production of large single crystals have made possible the investigation of the magnetic properties of single crystals of ferromagnetic metals. Iron (with a body centred cubic lattice) has been examined by Beck, Webster, Honda and Kaya, and Gorlach ; nickel (face centred cubic) by Sucksmith, Potter and Broadway and by Kaya.* There is agreement between the different investigators as to the general character of the results, but differences in detail, which are probably due to

* W. L. Webster, *Proc. Roy. Soc.*, 107, 496 (1925) ; K. Honda and S. Kaya, *Sci. Rep. Tohoku Univ.*, 15, 721 (1926) ; W. Gerlach, *Zeits. für Phys.*, 38, 828 (1926) ; 39, 327 (1926) ; 44, 279 (1927) ; W. Sucksmith and H. H. Potter, *Proc. Roy. Soc.*, 117, 471 (1928) ; S. Kaya, *Sci. Rep. Tohoku Univ.*, 17, 1 (1928).

the marked changes in the magnetic properties which may be caused by small amounts of impurity, and by different mechanical treatment.

In Webster's experiments discs some 4.5 mm. in diameter and .35 mm. thick, cut parallel to the (1, 0, 0) face were used. Saturation (intensity about 1,620) occurred in fields of about 1,000 gauss. No variation in the intensity parallel to the field for the same field in different directions was found except in the region just below saturation, where the maxima along the quaternary axes exceeded the minima along the diagonals by about 15 per cent. Although iron has a cubic structure there is a component of the magnetization perpendicular to the field, which also has a period of 90° , being zero when the field is along one of the crystallographic axes. This may be taken as indicating the presence of an internal magnetic field with a maximum value of about 600 gauss. This internal field is not the same as the Weiss molecular field whose value in any ferromagnetic must be very large. It is a hypothetical field to explain the differences in properties in different directions, and it has been shown by Mahajani * that it can be accounted for by the purely magnetic interaction of the elementary magnets arranged on the crystal lattice. The results on nickel are somewhat similar in character.

In Gerlach's experiments the specimens were in the form of cylindrical rods, in which there were single crystals sometimes as long as 3 cm. In some of these the crystal axes were inclined at very small angles to the axis of the rod, so that the magnetization curves for different axes could be obtained. Typical curves are shown in Fig. 17.

Along the digonal axis saturation (1710 ± 8) was attained at 600-800 gauss, along the tetragonal at about 150 gauss. The differences in the region just below saturation are in agreement with Webster's

* G. S. Mahajani, *Phil. Trans.*, 228, 63 (1929).

observations. The best specimens had a very high initial permeability and very small hysteresis; the remanent induction, B_r , along the digonal axis was in some cases less than 50, and the coercive field as small as .05 gauss. The results as a whole suggest that the Weiss domains cannot be identified with single crystals, but that the 'excellence' of a crystal depends on the degree of perfection with which the domains are joined

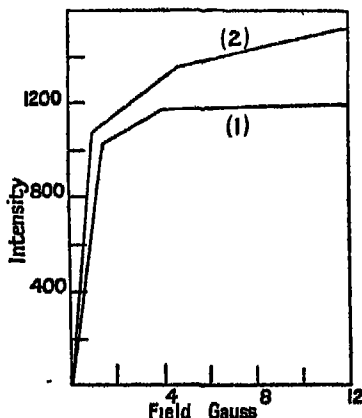


FIG. 17.—Variation of Magnetization with Field along the Digonal (1) and Tetragonal (2) Axis of a Single Iron Crystal

together. There is no marked direction of easy magnetization, as in pyrrhotite crystals, but the high initial permeability is in agreement with the view that there are domains throughout which there is spontaneous magnetization to the degree appropriate to the temperature. An ordinary crystal is full of imperfections, so that the properties observed may differ in important particulars from those of an ideal crystal, as imperfections of any kind may produce a large effect on the magnetic properties.

MAGNETO-MECHANICAL EFFECTS

Although an enormous amount of experimental work has been carried out on the change of length accompanying magnetization, and allied magneto-mechanical effects, for various ferromagnetics, it cannot be said, on the whole, that it has shed much light on the underlying nature of the magnetization process. This is partly due to the fact that investigations have for the most part been made on ordinary specimens which,

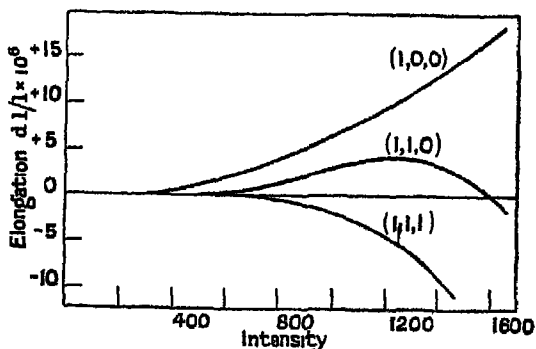


FIG. 18 — Change in Length with Intensity of Magnetization in a Longitudinal Field along the different Axes of an Iron Crystal

consisting of an aggregate of micro-crystals, have an ill-defined and varying structure. Investigations on the magneto-striction effects in single crystals, such as have recently been carried out by Webster,* and by Honda and Mashiyama,† promise to give much more definite and significant information.

The results of Webster for an iron crystal are shown in Fig. 18.

The elongation will obviously be more closely related to the intensity of magnetization than to the applied

* W. L. Webster, *Proc. Roy. Soc.*, 109, 570 (1925).

† K. Honda and Y. Mashiyama, *Sci. Rep. Tohoku Univ.*, 15, 755 (1926).

magnetic field. Along the (1, 0, 0) axis there is a continuous increase, along the (1, 1, 1) a continuous decrease in length. For the (1, 1, 0) axis there is at first an increase and then a decrease, the curve resembling that for soft iron. At high intensities the elongation is approximately a linear function of the intensity.

Nickel contracts in all fields, and it is of interest to note that while iron nickel alloys with more than 81 per cent. Ni contract, those with less than 70 per cent. expand, so that the high initial permeability of perm-alloy (78 per cent. Ni) is associated with a small or vanishing magneto-striction.

General dynamical considerations suggest that there should be a number of reciprocal relations, which have largely been verified. Thus it is found that the magnetization of nickel (which contracts when magnetized) is decreased by tension. For iron tension produces an increase in magnetization in weak fields and a decrease in strong, there being a reversal point corresponding to the magneto-striction reversal point.

The variety of effects observed with different ferromagnetics shows that magneto-striction cannot be due to the purely magnetic forces set up by magnetization. Magneto-striction and associated effects (such as the change in volume on passing through the Curie point) must be connected with the molecular field, and Fowler and Kapitza * have recently shown that the Heisenberg theory of ferromagnetism, in giving a quantum-mechanical explanation of the origin of the molecular field, covers satisfactorily, in a qualitative way, the various magneto-mechanical phenomena.

THE QUANTUM INTERACTION THEORY OF THE MOLECULAR FIELD †

The molecular field in ferro- and paramagnetics cannot originate in the purely magnetic interaction of

* R. H. Fowler and P. Kapitza, *Proc. Roy. Soc.*, 124, 1 (1929).

† W. Heisenberg, *Zeits. für Phys.*, 49, 619 (1928); see also R. H. Fowler and P. Kapitza, *Proc. Roy. Soc.*, 124, 1 (1929).

the carriers of the magnetic moment, and attempts to explain it as due to an associated electrostatic interaction have proved unsuccessful. In fact, on a classical basis, no satisfactory explanation could be found of those phenomena which are formally correlated by the molecular field hypothesis. The old quantum theory did little to remove difficulties, for its inadequacies were particularly apparent where interaction was concerned; the well known example being the interaction of the two electrons in the helium atom. Heisenberg showed that with the new mechanics a treatment of the helium atom could be given which, in essentials, was completely satisfactory. In the theory a new type of quantum resonance, corresponding to the interchange of the two electrons, plays an important part. Later, the Schrödinger methods were applied by Heitler and London to the problem of the hydrogen molecule. The possibility of the formation of a stable molecule was found to arise from an interchange interaction of the electrons in the two atoms, which has no classical counterpart. A great step forward in magnetism has been made by Heisenberg in showing that molecular field phenomena take their place in the quantum-mechanical scheme as arising from an interchange interaction of this kind. Although the details cannot be considered here, it seems desirable to give a brief indication of the general idea, which may be best approached by considering the interaction of two normal hydrogen atoms.

For a system consisting of two hydrogen atoms at a given distance apart, it is found that two different energies are possible, one corresponding to an attraction and the other to a repulsion. The difference in energy of the two states is large compared with the magnetic energy due to the electron spins. In the state of lower energy, in which the solution of the Schrödinger equation is symmetrical with respect to the co-ordinates of the electrons (ignoring the spins), the spins are antiparallel. It is this solution which corresponds to molecule forma-

tion. The difference in energy between this state and one in which only the ordinary electrostatic interaction of the two atoms is considered is due to a perturbation which arises from the fact that the electron in the first atom may also be regarded as forming part of the system of the second atom, and that of the second as forming part of the system of the first. There may be, so to speak, an interchange of identity between the electrons of the two atoms. This interchange interaction gives rise to a term in the complete expression for the energy of the form

$$J_0 = \frac{1}{2} \int \int \psi_k^\kappa \psi_k^\lambda \psi_l^\kappa \psi_l^\lambda \left(\frac{2e^2}{r_{k\lambda}} + \frac{2e^2}{r_{\kappa\lambda}} - \frac{e^2}{r_{k\kappa}} - \frac{e^2}{r_{\lambda\lambda}} - \frac{e^2}{r_{\lambda\kappa}} - \frac{e^2}{r_{\lambda l}} \right) d\tau_k d\tau_l. \quad (23)$$

where k, l refer to the two electrons, and κ, λ to the two nuclei. The ψ 's are the characteristic functions of the unperturbed systems, and the $d\tau$'s elements of the configuration space of the specified electrons. This new type of interaction is peculiarly characteristic of the new quantum mechanics, and is of the greatest importance in connexion with the formation of molecules and crystals.

With a view to elucidating the phenomena of ferromagnetism, Heisenberg has worked out the general effect of interchange interaction on the magnetic properties of a crystal consisting of a lattice of similar atoms, each with one interacting electron. These electrons only are supposed to contribute to the magnetization. Each state of the system as a whole is characterized by a definite spin moment $sh/2\pi$ depending on the number of unpaired electrons. Although it is not possible to specify the energy of all the states corresponding to a moment s , the mean energy of these states can be calculated. When an external field H is applied there will be an additional energy depending on the projection m of s along H . A complicated

statistical treatment is then necessary to determine the most probable value of m , and so of the magnetic moment. The result only will be quoted, in a form suitable for comparison with the Weiss equations for ferromagnetism (2 and 3).

The expressions are simplified by using a number of abbreviations.

n = total number of electrons.

n' = number of unpaired electrons.

$y = n'/n$.

$\alpha = \mu H/kT$ where μ is the magnetic moment of the electron.

$\beta = zJ_0/kT$ where z is the number of neighbours surrounding each atom, and J_0 an interaction integral of the type (23).

The two simultaneous equations determining the state of magnetization are then

$$y = \tanh x \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (24)$$

$$x = \alpha + \frac{y}{2} \left(\beta - \frac{\beta^2}{z} \right) + \frac{\beta^2}{4z} y^3 \quad . \quad . \quad (25)$$

To exhibit the relation of these to the Weiss equations (2 and 3), it should be noted that when the magnetization is due to electron spin, σ/σ_0 becomes equal to n'/n ($=y$), and, as there are only two directions for the spin, the Langevin expression $\coth \alpha - 1/\alpha$ has to be replaced by $\tanh \alpha$. When an external field is applied the Weiss equations, with the above abbreviations, would become

$$y = \tanh \alpha \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

$$\alpha = \alpha + \frac{N_0 \sigma_0^2}{mRT} y$$

$$\alpha = \alpha + \frac{NI_0 \mu}{kT} y \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

where I_0 is the saturation intensity of magnetization, so that NI_0 is the maximum molecular field, H_0 , say.

Comparing the two sets of equations, as a rough approximation

$$\frac{NI_0\mu}{kT}y = \frac{\beta}{2}y = \frac{zJ_0}{2kT}y$$

$$NI_0 = H_0 = \frac{zJ_0}{2\mu} \quad . \quad . \quad . \quad . \quad . \quad (28)$$

The molecular field is thus exhibited not as a field at all in the ordinary sense, but as a manifestation of the interchange interaction of the electrons, and as being proportional to its magnitude.

When there is no external field the Heisenberg equations (neglecting terms in y^3) become

$$y = \tanh x \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$x = \frac{1}{2} \left(\beta - \frac{\beta^3}{z} \right) y \quad . \quad . \quad . \quad . \quad . \quad (30)$$

The graphs of these equations are somewhat similar in form to those of Fig. 9. For spontaneous magnetization to occur the slope of (30) must be less than the slope of the tangent at the origin of (29). This gives

$$\beta - \frac{\beta^3}{z} \geq 2 \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The expression on the left is a maximum when $\beta = z/2$. As an approximation (since the y^3 term has been neglected), for ferromagnetism to occur the following condition must hold.

$$z/2 - z^2/4z \geq 2$$

$$z \geq 8 \quad . \quad . \quad . \quad . \quad . \quad (32)$$

Each atom in the lattice must have at least eight neighbours. This condition is satisfied by the ferromagnetic elements which, in the ferromagnetic state, have either face-centred or cube-centred cubic lattices.

The theory thus shows that the molecular field phenomena both in ferro- and para-magnetics may be attributed to interchange interaction, the value of θ in the Weiss

equation for paramagnetics $\chi = C/(T - \theta)$, or the Curie temperature in ferromagnetics being approximately proportional to the interaction. For ferromagnetism to occur it is necessary that J_0 should be positive, and in iron of the order of magnitude 10^{-13} erg (1/50 electron volts). For hydrogen atoms J_0 is essentially negative, but Heisenberg shows that for higher quantum numbers J_0 may be positive. He estimates that for this to occur the lowest total quantum number n of the interacting electrons must be about 3. This condition is again fulfilled by the ferromagnetic elements. It does not follow that J_0 is necessarily positive for high quantum numbers, as is shown by the fact that θ is negative for γ iron. The part of the theory concerned with the numerical magnitude of J_0 is as yet little developed owing to the mathematical difficulties. There is no explanation as to why ferromagnetism among elements is peculiar to only three of them. It should be noted that the interaction which affects the magnetic properties may be only a small part of the total interaction, as has been shown by Fowler and Kapitza. The model with one interacting electron per atom is of course much simpler than that corresponding to any actual ferromagnetic. In iron, for example, the saturation intensity and the change of specific heat at the Curie point show that there must be two or three electrons per atom concerned in the magnetic effects. These considerations show that the theory must be developed much further before it can be considered completely satisfactory; but there is a great advance in the elucidation of the significance in the general theoretical scheme of the hitherto baffling molecular field phenomena.

CHAPTER V

MAGNETIC PROPERTIES OF THE ELEMENTS

SUSCEPTIBILITY

THE magnetic properties of the ferromagnetic elements and of the inert gases have already been considered, and also those of some of the elements which exist at ordinary temperatures as gases, such as oxygen, nitrogen and chlorine. The most comprehensive investigation of the elements generally is that started by Honda* and continued by Owen.† The susceptibilities of some 60 elements were measured at temperatures ranging from that of liquid air to about 1,200° C. The elements were obtained in as pure a state as possible, and particular care was taken to eliminate errors which may arise from the presence of even small traces of iron. The results, supplemented by those of later workers, enable a survey of the magnetic properties of the elements to be made. The susceptibilities of many of the elements are very small, and as the results of different experimenters often differ considerably, it is only justifiable to regard the values quoted as correct as to order of magnitude for the pure elements. The relative values at different temperatures are probably more certain, and it is in this respect that the results are most remarkable. The susceptibility of many diamagnetic elements varies considerably with the temperature. Among paramagnetic elements the susceptibility of some is approximately constant, while that of others actually increases with increasing temperature.

* K. Honda, *Ann. der Phys.*, 32, 1027 (1910).

† M. Owen, *Ann. der Phys.*, 37, 657 (1912).

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In dia- and paramagnetics of the polar salt type the nature of the magnetic carriers is fairly well defined. The substances may be regarded as aggregates of quasi-independent ions, and to these the general theory as to susceptibility and its variation with temperature can be applied. It is, however, not legitimate to regard a metal simply as an aggregate of atoms with characteristics similar to those which they have in the free state. This is shown by the magnetic evidence itself, for paramagnetic atoms, such as copper and silver, may form a diamagnetic solid. In a metal there are free electrons, and there may be complex interchanges of electrons between the atoms. The effect of an increase of temperature on the magnetic properties may be very different from that on a substance in which the nature of the magnetic carriers is unchanged. It may, for example, produce a partial freeing of paramagnetic carriers from aggregates, this resulting in an increase in the paramagnetism as the temperature rises.

These considerations make it clear why there are no very simple or obvious periodic relations in the magnetic susceptibilities of the elements. Each element presents a separate problem. Only a brief general survey of the results will be given here, the elements being ordered in accordance with their periodic positions. If particular groups of elements are considered some regularities do emerge. (Elements are followed by their atomic numbers. Where stated the susceptibilities given are $\chi_A \times 10^6$.)

The transition elements Ti (22)—Mn (25), Mo (42)—Pd (46) and La (57)—Pt (78) are paramagnetic. Among these the rare earths, Pt and Pd roughly follow a Weiss law with a large negative value for θ . They give approximate magneton values of the same order of magnitude as those found for normal paramagnetics.—Pd 9.7, Pt 10, Ce 11, Pr 14.5, Er 14.5.

In the first group Na (11), K (19), and Rb (37) have a small constant paramagnetism; Cs (55) is diamagnetic. Cu (29), Ag (47) and Au (79) are diamagnetic, the sus-

ceptibility increasing with increasing atomic number from -5.4 (Cu) to -29.6 (Au).

The elements of the Mg group, with the doubtful exception of Sr, are paramagnetic, Ca (20) having a constant susceptibility of about $+44$. Zn (30), Cd (48) and Hg (80) are increasingly diamagnetic.

Al (13) has a varying paramagnetism, but Ga (31), In (49) and Tl (81) are diamagnetic, the diamagnetism decreasing with increasing temperature.

The elements of the fourth group (C — Pb) are diamagnetic, except for one form of Sn (50). While grey tin is diamagnetic, the white tetragonal variety is paramagnetic. The values for the different allotropic forms of carbon differ considerably.

As (33) Sb (51) and Bi (83) are diamagnetic. The susceptibility of Bi is very high (-293) and it decreases linearly with temperature up to the melting point (273°C.); at the melting point the susceptibility diminishes abruptly to about -8 , and then remains constant.

S (16), Se (34) and Te (52) are increasingly diamagnetic and also Br (35) and I (53).

In general the mass susceptibilities of the diamagnetic elements lie between -10^{-7} and -10^{-8} , and in families of diamagnetic elements, the atomic susceptibility increases with increasing atomic number. On the theory developed in the chapter on diamagnetism the values indicate a root mean square radius for the electronic orbits ranging from about $.3$ to $.9 \times 10^{-8}$ cm.—a reasonable order of magnitude. The high susceptibility of bismuth, however, has led to the suggestion, by Ehrenfest, that electron orbits may sometimes encircle two or more nuclei. As the temperature rises the aggregates break up, and the liquid has a much lower susceptibility, suggesting that the electrons then encircle only a single nucleus. The electron orbit interpretation can, of course, readily be restated in terms of the space charge distribution conception of the atom.

In a solid element there may be present both dia-

magnetic and paramagnetic systems, and if these change with changing temperature, many of the general results for the elements can be tentatively explained in terms of the usual theory in a qualitative manner—though a detailed interpretation of the results for particular elements would require much further investigation. There is one outstanding fact, however, which does require further explanation, namely the occurrence, in some elements, of an approximately constant paramagnetism which is considerably smaller than that of any normal paramagnetics. Pauli has shown that this may be due to the peculiar characteristics of aggregates of free electrons indicated by quantum statistical theory.

THE PARAMAGNETISM OF FREE ELECTRONS

Theory.—Metallic conduction at once receives a general explanation on the assumption that there are free electrons present in metals. The number of electrons required, however, is of the same order as the number of atoms, and a serious difficulty was encountered in that they apparently made practically no contribution to the specific heat. The spectroscopic facts indicate that the electron has a magnetic moment, so it would seem too that metals should be paramagnetic; yet the susceptibility results show that the paramagnetism of the 'electron gas' must certainly be very small.

These difficulties have been resolved by an elegant application of the Fermi statistics to the electron gas. Sommerfeld has shown that the contribution to the specific heat at ordinary temperatures will be negligible, and Pauli * has calculated the paramagnetism and shown that it will be small and approximately constant. The argument will be outlined, but for details of the calculations reference must be made to the original papers.

* W. Pauli, *Zeits. für Phys.*, 41, 81 (1927). For a simple, but less general derivation of the susceptibility formula, see J. Frenkel, *Zeits. für Phys.*, 49, 31 (1928).

The number of electrons in the different quantum groups of an atom is limited. The possible number may be deduced from the Pauli principle that there cannot be more than one electron with a specified set of four quantum numbers (n , l , m_l and m_s), or that there cannot be more than two with the same set of three quantum numbers specifying the orbital motion (n , l and m_l). The possibility of two arises from the fact that there are two possible directions for the spin ($m_s = +\frac{1}{2}$ or $-\frac{1}{2}$). In an atom, then, there cannot be more than one electron in one particular state. (The wave mechanical formulation of the Pauli principle is different, but the content is the same.) This limitation on the number of electrons in definite states in atoms has been extended by Fermi to the case of similar mass particles in an enclosure. The Fermi statistics is based on a limitation on the number of similar mass particles in a given volume with momenta within a given range.

The quantization of translatory motion is least artificially approached by considering the wave aspect of mass particles. The wave length associated with a mass particle of momentum p ($p = mv$) is given by $\lambda = h/p$. Now the number of possible stationary vibrations in a volume V with wave length in a range $d\lambda$ is equal to $V \cdot 4\pi\lambda^{-4} d\lambda$. Correspondingly (substituting h/p for λ) the number of possible values of the momentum in a range dp is equal to $V \cdot 4\pi p^2 dp / h^3$. According to the Fermi limitation, this gives also the maximum number of similar particles with momenta in this range; otherwise expressed, there cannot be more than one particle (of statistical weight 1) in each unit cell h^3 of the 6-dimensional phase space, so that there cannot be more than 1 particle with momentum in a range dp such that

$$4\pi p^2 dp = h^3 / V \quad . \quad . \quad . \quad (1)$$

Electrons, with two directions of spin, have a statistical weight 2, and there cannot be more than 2 electrons in

this range. At absolute zero the electrons in the 'electron gas' in a metal will have the lowest possible energy and will congregate in the cells corresponding to the lowest possible momenta. Let N be the number of electrons in the volume V (n per unit volume); these will congregate in pairs in the Z lowest cells, where $Z = N/2$. On the above basis the mean energy of the electrons at absolute zero may be shown to be

$$\bar{\epsilon}_0 = \frac{3}{40} \frac{h^2}{m} \left(\frac{3n}{\pi} \right)^{2/3} \quad . \quad . \quad . \quad (2)$$

The relation between the energy ϵ_0 of the electrons in the highest cell at absolute zero and the mean energy $\bar{\epsilon}_0$ is

$$\epsilon_0 = \frac{5}{3} \bar{\epsilon}_0 \quad . \quad . \quad . \quad (3)$$

Since the factor $\frac{1}{m}$ enters into the expression for $\bar{\epsilon}_0$ the

minimum energy of an aggregate of electrons is much greater than that of an aggregate of atoms. The mean energy of electrons at a concentration equal to that of atoms in metals will be of the same order as that of the atoms of a classical gas at about 10,000 degrees; it will change little with temperature, and at ordinary temperatures the electron gas may still be treated as completely 'degenerate' as at absolute zero.

The process of magnetization consists in a reversal in the direction of the magnetic moment of some of the electrons, which, in the absence of a field, are balanced in pairs. Since there cannot be more than one electron in each cell with its spin moment parallel to the field, magnetization necessarily involves the removal of electrons to cells corresponding to higher energy. The process can only continue as long as the change in magnetic energy is sufficient to balance the necessary increase in kinetic energy. Let $\Delta\epsilon$ be the difference in energy of electrons in successive cells in the region

of maximum momentum ; let μ be the magnetic moment of the electron, and let x be the number of electrons removed from the initially highest x cells, to the x successive higher ones. For the x^{th} electron the change in magnetic energy is equal to the change in kinetic energy.

$$2x\Delta\varepsilon = 2\mu H \quad . \quad . \quad . \quad (4)$$

The total magnetic moment is then $2x\mu$, and the volume susceptibility, κ , is given by

$$\kappa = \frac{2x\mu}{VH} = \frac{2\mu^2}{V\Delta\varepsilon} \quad . \quad . \quad . \quad (5)$$

$\Delta\varepsilon$ may be shown to be equal to $\frac{4}{3} \frac{\varepsilon_0}{N}$

$$\begin{aligned} \kappa &= \frac{3\mu^2 N}{2\varepsilon_0 V} = \frac{3\mu^2 n}{2\varepsilon_0} = \frac{9}{10} \frac{\mu^2 n}{\varepsilon_0} \\ &= 12\mu^2 n^{1/3} \frac{m}{\hbar^3} \left(\frac{\pi}{3}\right)^{2/3} \quad . \quad . \quad . \quad (6) \end{aligned}$$

Substituting $eh/4\pi mc$ for μ , and inserting numerical values, this gives

$$\kappa = 2.209 \times 10^{-14} n^{1/3} \quad . \quad . \quad . \quad (7)$$

The theory, then, indicates that the paramagnetism due to free electrons will be small and that for n constant it will vary little with temperature. For metals with a number of free electrons equal to the number of atoms (of the order of 10^{23} per c.c.) the calculated volume susceptibility is of the order of 10^{-6} .

Comparison with Experiment.—Pauli has calculated the susceptibility of the electron gas in the alkali metals on the assumption that there is one free electron per atom. The remaining positive ions, however, will then make a diamagnetic contribution to the susceptibility, and it seems desirable that some allowance should be made for this, even if it can only be done roughly. In the following table the gram atomic susceptibility χ_A is calculated as the sum of the gram electronic

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susceptibility χ_a (from 7) and that of the positive ions χ_{A+} , obtained from Ikenmeyer's results (Table I, Chapter II). McLennan's results show that the susceptibilities of the alkali metals are approximately constant from room temperature down to -190°C . At the melting point there is an abrupt but small decrease, and above a gradual increase in the susceptibility with temperature (Sucksmith). The values in the table are those at 0°C .

TABLE XIV.

Calculated and Observed Susceptibilities of Alkali Metals
 $\chi_A \times 10^3$.

	Na	K	Rb	Cs
χ_E Calo.	15.6	23.6	27.2	32.3
χ_{A+} Obs.	-10.4	-16.9	-31.3	-45.7
χ_A Calo.	6.2	6.7	-4.1	-13.4
χ_A Obs. { II^*	12	16	6	-13
S^\dagger	14	20	6	-7
M^\ddagger	14	19	17	28

No very close agreement between the calculated and observed values would be expected. The calculated value of χ_E depends on the assumption made as to the number of free electrons, but so long as the number does not differ greatly from 1 per atom χ_E (depending on $n^{1/3}$) will be approximately correct. It is only if there is one free electron per atom, however, that the diamagnetic contribution of the ions be can estimated

* K. Honda and M. Owen, *l.c.*

† W. Sucksmith, *Phil. Mag.*, 2, 21 (1926).

‡ J. C. McLennan, R. Ruedy and E. Cohen, *Proc. Roy. Soc.*, 116, 468 (1927).

and the ions in the metal will certainly not have exactly the same charge distribution as the ions in a polar salt. As was seen before, the diamagnetism of the ions in salts is not accurately known; for Na^+ , in particular, the true value is probably smaller than $10 \cdot 4$ (see Table IV, Chapter II), and this would bring the calculated and observed values of χ_A into closer agreement. Finally the observed values of χ_A differ considerably, this being partly due to the difficulty of estimating exactly the effect of impurities. The results of Honda and Sucksmith are in agreement in indicating that Rb is less paramagnetic than K, and that Cs is diamagnetic. As the calculated values of χ_D differ little, this fits in with the view that there are both dia- and para-magnetic effects, the diamagnetic effect increasing with increasing atomic number. The idea of free electrons is rather a loose one. In a metal the so-called free electrons must interact to some extent with the ions, and in a complete theory this interaction will have to be taken into account. Still, the results as a whole show that Pauli's theory of the paramagnetism of free electrons in its present form is a valuable contribution towards the understanding of some of the puzzling features of the susceptibilities of elements.

THE CHANGE OF ELECTRICAL CONDUCTIVITY IN STRONG MAGNETIC FIELDS

Among the most remarkable achievements in physical research in recent times is that of Kapitza, at the Magnetic Laboratory at Cambridge, in developing a method of obtaining very strong magnetic fields and investigating their effect on atomic phenomena. It is beyond the range of this book to describe the elaborate technique,* but a brief account will be given of the results on the effect of strong fields on the conductivity of elements. In order to obtain a strong field it is

* P. Kapitza, *Proc. Roy. Soc.*, 115, 658 (1927).

necessary to have a large current flowing in a coil. The overheating which would normally occur is avoided by allowing the current—obtained by short circuiting a specially constructed A.C. generator of the turbo-alternator type—to flow only for a very short time, about a hundredth of a second. Technical difficulties connected with the switches, the timing arrangements, and the construction of coils to withstand the enormous strain set up have been successfully overcome. Fields up to 350,000 gauss over a volume of about 2 c.c. have been used—about 7 times greater than those obtainable with the most powerful electromagnets over considerably smaller volumes—and larger fields are possible. In determining the electrical conductivity in magnetic fields, the current through the specimen and the potential difference across it, together with the current through the coil (giving the magnetic field) are observed by oscillographic methods, the three curves being recorded on a single plate.

After a detailed investigation of bismuth,* a systematic survey was made of some 35 elements.† For impurities to have only a small influence, a purity of at least 99.9 per cent. was essential. The change in resistance in fields up to 320 kilogauss transverse to the current was measured at room temperature (290° A.), at the temperature of solid CO₂ and ether (193° A.), and at the temperature of liquid nitrogen (88° A.), and it was also measured in parallel fields for a few elements. The general character of the results is indicated by the curves shown for magnesium.

For the weaker magnetic fields (below a certain critical value H_L), the relative change in resistance is proportional to the square of the field—as had been found by previous investigators. In stronger fields, however, the resistance change increases linearly with the field. Within the limits of experimental error the results may be expressed by the following formulae—

* P. Kapitza, *Proc. Roy. Soc.*, 119, 358 (1928).

† P. Kapitza, *Proc. Roy. Soc.*, 123, 292 (1929).

$$\frac{\Delta R}{R} = \beta \frac{H^2}{3H_i} \quad \text{for } H < H_i \quad . \quad . \quad (8a)$$

$$\frac{\Delta R}{R} = \beta \left(H - H_i + \frac{H_i^2}{3H} \right) \quad \text{for } H > H_i \quad . \quad . \quad (8b)$$

The critical field varies, for different elements, between 5 and 250 kilogauss. The physical state of a conductor, depending on the hardening or annealing processes it

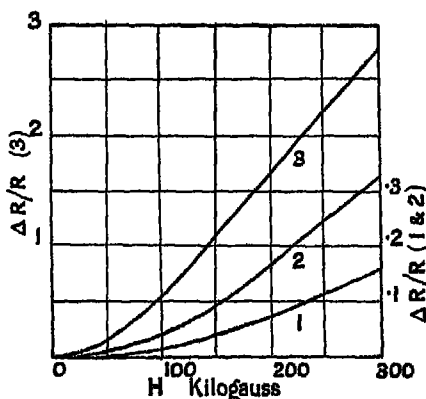


FIG. 19.—Change of Resistance of Magnesium in a Transverse Magnetic Field
(1) 290° Abs. (2) 193° Abs. (3) 88° Abs.

has undergone, produces a marked effect, but the important fact emerges that it influences only H_i , leaving β practically constant.

The theory put forward by Kapitza is based on the view that the linear law is the ideal law of change of resistance, but that this is masked in small external fields owing to an initial disturbance in the metal. This disturbance may be treated as equivalent to that produced by an initial field h distributed at random; the field h being equivalent in its effects to a magnetic field, though not necessarily magnetic in origin. (It seems probable that

the effects are connected with quantum interchange energy, as in Heisenberg's theory of ferromagnetism.) Let $\beta_p h$ be the change in resistance due to a field h parallel to the current, and $\beta_n h$ that due to a field normal to the current.

$$h \parallel I \quad \Delta R/R = \beta_p h \quad . \quad . \quad . \quad (9a)$$

$$h \perp I \quad \Delta R/R = \beta_n h \quad . \quad . \quad . \quad (9b)$$

For a field h distributed at random the ratio of the 'additional resistance' ΔR_0 to the 'ideal' resistance R_i will then be given by

$$\Delta R_0/R_i = \frac{1}{2}(2\beta_n + \beta_p)h \quad . \quad . \quad . \quad (10)$$

The observed resistance is equal to the sum of the ideal and additional resistance

$$R = R_i + \Delta R_0 \quad . \quad . \quad . \quad (11)$$

To determine the effect of an external field H it is necessary to calculate the resultant effect of the vectorial sum of \vec{H} and the randomly distributed h . The results will differ according to the relative magnitudes of β_n and β_p . Where these have both been measured they do actually differ, but their ratio is such that the general character of the results is the same as that obtained by assuming them to be equal. This assumption gives a simple limiting case, the consideration of which brings out the main points. Let $\beta_n = \beta_p = \beta_0$. The calculation then gives

$$\Delta R/R_i = \beta_0 H^2/3H_i \quad H < H_i \quad . \quad . \quad (12a)$$

$$\Delta R/R_i = \beta_0 (H - H_i + H_i^2/3H) \quad H \geq H_i \quad . \quad . \quad (12b)$$

where $H_i = h$. These equations are the same as those found experimentally (8) except that R_i and β_0 take the place of R and β . The variation with field is shown in Fig. 20.

For the asymptote of the curve

$$\Delta R'/R_i = \beta_0 (H - H_i) \quad . \quad . \quad . \quad (13)$$

or substituting from (10)

$$\Delta R'/R_i = \beta_0 H - \Delta R_0/R_i \quad . \quad . \quad . \quad (14)$$

The intercept of the asymptote on the H axis therefore gives H_k , equal to the initial field h ; and the intercept on the $\Delta R/R$ axis, the ratio of the additional to the ideal resistance. Using (11) and noting that $\beta_0 R_i = \beta R$, the theoretically significant constants β_0 and R_i can readily be obtained from the observed values of β , H_k and R .

The experimental results enable the ideal resistance to be separated from the additional resistance. It is found that the variation in resistance of differently

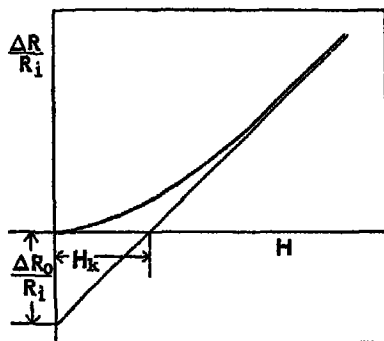


FIG. 20.—Diagram showing the Significance of the Intercepts made by the Asymptote to the Resistance-field Curve

treated specimens is almost entirely due to variations in the additional resistance. For two specimens of gold, for example, one soft and the other hard, the specific resistances σ at liquid nitrogen temperatures (10^{-8} units) were $\cdot 487$ and $\cdot 520$; the additional resistances were $\cdot 035$ and $\cdot 064$, the ideal resistances σ_i being practically the same, $\cdot 452$ and $\cdot 456$. The additional resistance varies little with temperature, but the ideal resistance decreases continuously as the temperature is lowered, and at a sufficiently low temperature it has immeasurably small values. A comparison of the data indicates that the additional resistance is identical with the

'residual' resistance of Onnes—this being the practically constant resistance reached by most metals for the last 10 or 20 degrees approaching absolute zero. Kapitza suggests that supra-conductivity is due to the disappearance (for some unknown reason) of the additional resistance, and that it is quite possible that supra-conductivity would be found in all metals if they could be obtained in a sufficiently pure and undisturbed state.

From the coefficient β , the absolute increase in resistance per atom $\Delta\sigma_a$ in the undisturbed metal in a field of 1 gauss may be calculated, and this is probably of greater significance.

$$\Delta\sigma_a = \beta_0 \sigma_a A / \rho \quad . \quad . \quad . \quad (15)$$

The values of $\Delta\sigma_a$ apparently tend to a limit as absolute zero is approached, but experiments have not yet been carried out at low enough temperatures to determine these limiting values. The indications are that $\Delta\sigma_a$ is of the same order of magnitude in each group of elements, being smallest in the first group (at 88° abs., $\Delta\sigma_a \times 10^{12} = 5.8$ for Au) and rising to a maximum towards the middle of the periodic table. The resistance increase of most of the transition elements is small.

Small amounts of impurities give rise, like physical distortion, to an increase in the critical field; that is to say, they are associated, on the view described, with an increase in the initial disturbing field. A large amount of impurity, as in an alloy, produces a similar effect to an increase in temperature—it produces an increase in R_c and a decrease in β_0 . A definite metallic compound, such as Cu_3As , in which the atoms are arranged regularly, behaves like a pure metal.

It should be noted that the theory cannot be applied without modification to semi-conductors, such as Ge and Te, and to the associated elements As, Sb, and Bi. In these the resistance increase ($\Delta\sigma_a$) is very much greater. It is suggested that there are what may be

roughly described as 'tight' and 'loose' bonds round the atoms (the loose bonds being those associated with conduction electrons) and that the magnetic field has a second effect in disturbing the equilibrium between these.

The essential fact which emerges from these investigations is that, ideally, the change in resistance is proportional to the field. In all the theories which have previously been put forward, the change of resistance, as calculated from the effect of the field on the motion of the electrons, is proportional to the square of the field, and is much smaller than that found experimentally. Kapitza suggests that the effect of the field is to change the scattering power for electrons of the individual atoms. It is known from the Ramsauer effect that the scattering power depends on the symmetry of the atoms, that of inert gas atoms being very small. The magnetic field may disturb the symmetry of the atoms, increasing their scattering power, and so increasing the resistance.

The hypothesis of an initial disturbing field is fully justified by its success. If it is equivalent in its effect to a magnetic field it may have an important bearing on the problem of the susceptibilities of the elements, for the magnetic moment (and so the observed susceptibility) will depend on the initial as well as on the applied field. The large effect of impurities in modifying the initial field may account for the lack of agreement in the susceptibility results of different observers.

The value of a strong magnetic field as a weapon of attack on atomic problems is shown by Kapitza's work. It not only sheds an entirely new light on electrical conduction, but it provides an enormous amount of information about the properties of a large number of elements and the effect of impurities on them. In connexion with the change of electrical conductivity in magnetic fields, much further experimental work remains to be done, and much of the theoretical treat-

ment is very tentative. The interest of an investigation, however, lies not only in what has been achieved, but also in the incentive it gives towards further inquiry.

CONCLUSION

IN reviewing the state of magnetism towards the end of 1925, it was suggested that there were three outstanding problems—'Perhaps the outstanding magnetic problems are those connected with the gyromagnetic anomaly, the mechanism of orientation, and the nature of internal fields. The first is related to the difficulty of giving a physically significant treatment of the Zeeman effect; the second to the super-mechanical tendency of systems to assume quantum stationary states; and the third to the general problem of crystal structure and stability.'* To a certain extent, all these problems have now been solved, in the sense that the phenomena concerned no longer appear as particular anomalies, but are covered by the general theoretical scheme. The gyromagnetic anomaly, and many of the peculiarities of the Zeeman effect could be explained on the assumption that the electron had a definite mechanical and magnetic moment; and the empirically necessary values of these were later shown to follow from the requirement that the equations of motion of the electron must satisfy conditions imposed by relativity and quantum mechanics. The quantum mechanical conception of the atom is much less definite than the orbital conception, and the problem of orientation, and of the time required for orientation, no longer arises in the old form. The idea of orientation or change of orientation implies a quasi-rigid body. With the new conceptions, a definite orientation must be interpreted as meaning simply a definite distribution of charge or of 'probability'. With respect to the time required for orientation in a field, the principle of indefiniteness,

* *Magnetism and Atomic Structure*, p. 355.

of which quantum mechanics provides a quantitative formulation, shows that the determinateness of orientation (or of energy depending on orientation) depends on the interval of time to which the determination applies, the dependence being such as to remove the former difficulties. There is no counterpart in the older quantum theory to the interchange interaction of electrons in different atoms which plays an important part in the new quantum mechanics. While the theory is still incomplete, it is fairly certain that the effects attributed to the hypothetical molecular field are due to this quantum interaction. The first step towards the elucidation of related problems as to the structure and stability of aggregates of atoms is provided by the quantum mechanical treatment of simple molecules.

Among the problems referred to, those connected with molecular fields have been by no means completely cleared up; but whereas a few years ago the molecular field could not be explained at all, it is now seen as a particular example of a more general phenomenon. It is in the further development and application of quantum mechanics that a fuller understanding of the magnetic properties of materials must be sought.

In matters of detail magnetism presents a large number of experimental and theoretical problems, as will be apparent from the topics which have been dealt with in this book. To mention an obvious example on the experimental side, the susceptibility data for many dia- and para-magnetics are very uncertain, and none are available at all for many substances whose magnetic characteristics would be of great interest. The exact significance of the values found for the moments of many paramagnetic ions, and of their variability, is by no means clear. There is no satisfactory theory as to why ferromagnetism appears in such a limited number of substances, while practically the whole of the detailed behaviour of ferromagnetics, thermal and mechanical, as well as magnetic, requires further investigation and explanation.

It is by the investigation of details that science progresses, but it is to the linking together of details that it owes its strength. This account of a restricted range of magnetism has illustrated the two processes, and has indicated how far magnetic phenomena fit into a wider systematic symbolical scheme.

NOTE ON BOOKS AND ARTICLES

For the fundamental principles, any good text-book on Electricity and Magnetism, such as Starling's or Pidduck's, may be consulted; for the mathematical theory, Jeans' *Electricity and Magnetism*.

A rather more general account of Magnetism than that given here, with sections on the history and on magnetic measurements, will be found in the *Encyclopædia Britannica* (1929).

For particular topics the following are suggested:

- D. W. Dye, *Magnetic Measurements in A Dictionary of Applied Physics* (1922).—Measurements, and properties of ferromagnetics.
- E. C. Stoner, *Magnetism and Atomic Structure* (1926).—Experimental and theoretical work on dia- and para-magnetism, the Zeeman effect, etc.
- W. Peddie, *Molecular Magnetism* (1929).—Magnetic properties of crystals.
- T. F. Wall, *Applied Magnetism* (1926) and T. Spooner, *Properties and Testing of Magnetic Materials* (1927).—Technology.

There are chapters dealing mainly with atomic magnetism in E. N. da C. Andrade, *The Structure of the Atom* (1927) and H. A. Wilson, *Modern Physics* (1928).

In French there is a short outline by P. Weiss and G. Foëx—*Le magnétisme* (1926).

In German there is an excellent article by P. Debye—*Theorie der elektrischen und magnetischen Molekulareigenschaften*—in the *Handbuch der Radiologie*, Vol. VI (1925), while there is a comprehensive survey of the whole subject by various writers in the *Handbuch der*

Physik, Vols. XV and XVI (1927). Vol. XVI has articles on measurements, and Vol. XV on the magnetic field, on dia- and para- and ferromagnetism, and on ferromagnetic materials, the last being of particular interest.

A comprehensive collection of numerical data on magnetism is given in the *International Critical Tables*, Vol. VI, pp. 345-441 (1929).

For further details of the developments of the last few years, reference must be made to the original papers. The annual index to *Science Abstracts* provides a bibliography.

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